CRYSTAL STRUCTURES AND PHASE TRANSITIONS IN THE RARE EARTH OXIDES

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ACKNOWLEDGEMENTS

DECLARATION

The research in this thesis is my own work with the following exceptions.

All XRPD data collected on the Siemens and Bruker machines were performed by Geoff Parr of Salford Analytical Services.

Sample (7) of Yb_2O_3 was annealed by Zhenggang Lian of Southampton University.

The XRPD pattern obtained at Diamond Light Source was collected on beamline I11 by Professor Chiu Tang.

The DSC data represented in figure 8.5 was collected by Phil Williams of Mettler Toledo.

ABSTRACT

The lanthanoid sesquioxides exhibit a number of distinct structural phases. Below 2000°C these oxides exist in three crystal systems, namely the A-type hexagonal phase, the B-type monoclinic phase and the C-type cubic phase. With increasing temperature the stability of these structures is generalised by the order C → B → A, although not every oxide will exhibit all phases; this general transition is typical of the middle members of the group. Under ambient conditions, the A phase is preferred for La_2O_3 to Pm_2O_3. Both the C and B phases exist for Sm_2O_3, Eu_2O_3 and Gd_2O_3. The C phase is stable at room temperature from Sm_2O_3 onwards, and at the high atomic number end of the series this phase is preferred.

Traditionally, the structures of the heavier sesquioxides (Er_2O_3 to Lu_2O_3) have been believed to be cubic from ambient temperature all the way up to their melting points. However, contrary to the current phase diagram, my work has shown that not only are B-type Sm_2O_3, Eu_2O_3 and Gd_2O_3 very stable at ambient temperature, but it is also possible to create 1% monoclinic Yb_2O_3 by heating and then quenching back to ambient temperature.

Of the lanthanoids, praseodymium and terbium are known for their existence in both the +3 and +4 oxidation states. The praseodymium-oxygen system is notable for its multiple stoichiometries. This work presents kinetic data for the $\phi \rightarrow \beta$ phase and the $\sigma \rightarrow \theta$ phase transitions in this system, the results obtained via high-temperature X-ray powder diffraction and differential scanning calorimetry.

The crystal structures of B-type Gd_2O_3 and Yb_2O_3 are reported, the former obtained using both laboratory and synchrotron X-ray data and the latter using laboratory data alone. It is proposed that this is the first time these two structures have been determined following the application of temperature alone, without the additional application of pressure.

DEDICATION

For Phyllis Margaret Skinner

Told you I'd get there one day

1 INTRODUCTION

1.1 THE RARE EARTHS

The rare earths constitute a series of highly electropositive elements occupying period 6 of the periodic table between the 6s and 5d blocks and their occurrence marks the first occupying of the 4f atomic orbitals in the ground state. Unlike the d block elements their chemistry is fairly uniform across the series, with the +3 oxidation state dominating.

The series corresponds to the filling of the 4f atomic orbitals from lanthanum, which has an electronic configuration $[Xe]5d^16s^2$, to lutetium, $[Xe]4f^{14}5d^16s^2$. As the members of the series have similar properties they are referred to in the IUPAC scheme as the *lanthanoids*, after the first element in the series, lanthanum, which itself takes its name from the Greek $\lambda\alpha\nu\theta\alpha\nu\varepsilon\iota\nu$ (lanthanein), meaning *to lie hidden*. Despite this, the term *lanthanides* is still widely in use. All the lanthanoids have similar chemical properties, since the 4f atomic orbitals are of a smaller radial extension than the 6s and 5d atomic orbitals in which the valence electrons lie and hence do not greatly affect the chemistry of the elements. The f orbitals are said to be buried inside the atom and shielded from its external environment by the valence electrons. This means that the chemistry of the lanthanoids is largely determined by their atomic radii.

All the lanthanoids show the +3 oxidation state. An unusual deviation from this is seen with cerium, which can exhibit the +4 state, achieving the electronic stability of the noble gas xenon. Europium exhibits the +2 state, achieving the stability of a half-filled f shell. The +4 oxidation state is also seen with praseodymium and terbium. The element promethium does not occur in nature.

Although not actually lanthanoids, yttrium and scandium are often considered to be rare earths as they occur in the same sources. Yttrium, $[Kr]4d^15s^2$, is the immediate vertical neighbour of lanthanum, has a similar electronic configuration and shows a great chemical resemblance to the lanthanoids. The radius of its tripositive ion lies between those of Ho^{3+} and Er^{3+} and, as might be expected, its chemistry resembles these

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elements more strongly than it does any of the other lanthanoids. Scandium, $[Ar]3d^14s^2$, the lightest member of the transition elements and again vertical to lanthanum, also resembles the lanthanoids closely in its chemical properties.

The term *rare earths* is actually a misnomer. Cerium is the twenty-fifth most abundant element in the earth and is as common as copper. Even the least-common rare earth, thulium, occurs in greater proportion than mercury. However, because the rare earths have a similar chemistry and tend to occur naturally together, historically their separation from each other has been difficult. It is this fact that has given the impression of their rarity. The phrase *to lie hidden* indicates that the metals are difficult to separate i.e. they lie hidden behind each other. Originally, separation was performed by a laborious series of fractional crystallisations. As the lanthanoid ions have subtly different radii, the lattice energies of their salts and their hydration energies are also different. This means that they have slight differences in solubility and hence different metal salts will precipitate from solution at slightly different concentrations. In recent times, separation of ions has been achieved by solvent extraction and ion exchange. Both methods rely on the small differences in ionic radii across the group.

Typical sources of rare earths are monazite sand, the mineral xenotime (which both contain a mixture of the phosphates of lanthanoids and thorium) and bastnaesite (which contains lanthanoid fluorocarbonates). In terms of their occurrence in the earth's crust, lanthanum, cerium and neodymium are by far the most common. The rare earths have many applications. Their most common use is in catalytic converters for internal combustion engines. They also have use as refining catalysts in the petrochemical industry. Other uses include alloying material in permanent magnets, colours for glass and ceramics, phosphors, and doping agents for lasers. Cerium is contained in the alloy known as misch metal, used as the flint of cigarette lighters. It is also used as an anti-knock agent in petrol. Europium is used within nuclear fuel control rods and also within the red phosphor in CRT television screens. Ytterbium has been shown to have an application in thermophotovoltaic devices (Krishna *et al* 1999) and a lanthanum-doped sodium tantalate catalyst has recently been shown to be effective in the photolysis of water as a means of generating hydrogen fuel (Kato *et al* 2003).

1.2 THE STABILITY OF THE TRIPOSITIVE OXIDATION STATE

The ground state electronic configurations of the uncharged lanthanoid atoms and their tripositive ions are given in table 1.1. For the atoms, the 4f orbitals are generally more stable than the 5d, illustrated by the fact that the 5d orbitals are only occupied in a few cases. After lanthanum the 5d orbitals are empty and only when gadolinium is reached is the extra stability of the half-filled 4f orbitals sufficient to induce reoccupation of the 5d orbitals. For the tripositive ions, chemically the most important oxidation state, the 4f orbitals are much more stable and the 5d and 6s orbitals are not occupied at all. The electron configurations of the tripositive ions reveal a sequential filling of the 4f atomic orbitals from lanthanum at f^0 to lutetium at f^{14}.

The 4f electrons occupy space inside the $n = 5$ shell. They are more stable and have greater ionisation potentials than the 5d and 6s electrons. Consequently the loss of the 6s and 5d electrons is always seen before that of the 4f electrons. This is illustrated by electronic absorption spectra of compounds of tripositive lanthanoid ions. As a general trend, ionisation energy increases with atomic number and shows marked half-shell effects. Table 1.1 lists both the sum of the first three ionisation potentials and the fourth ionisation potential for the lanthanoids. These values are plotted in figure 1.1.

Z	Element	Electron config.	Electron config. for Ln^{3+}	Ionic radius (pm) 6CN[†]	ΣIP_{1-3}[*] kJ.mol^{-1}	IP_4[**] kJ.mol^{-1}
57	La	$[Xe]5d^16s^2$	f^0	117.2	3455	4819
58	Ce	$[Xe]4f^15d^16s^2$	f^1	115	3523	3547
59	Pr	$[Xe]4f^36s^2$	f^2	113	3627	3761
60	Nd	$[Xe]4f^46s^2$	f^3	112.3	3697	3899
61	Pm	$[Xe]4f^56s^2$	f^4	111	3740	3966
62	Sm	$[Xe]4f^66s^2$	f^5	109.8	3869	3994
63	Eu	$[Xe]4f^76s^2$	f^6	108.7	4036	4110
64	Gd	$[Xe]4f^75d^16s^2$	f^7	107.8	3749	4245
65	Tb	$[Xe]4f^96s^2$	f^8	106.3	3791	3839
66	Dy	$[Xe]4f^{10}6s^2$	f^9	105.2	3911	4001
67	Ho	$[Xe]4f^{11}6s^2$	f^{10}	104.1	3924	4101
68	Er	$[Xe]4f^{12}6s^2$	f^{11}	103	3934	4115
69	Tm	$[Xe]4f^{13}6s^2$	f^{12}	102	4045	4119
70	Yb	$[Xe]4f^{14}6s^2$	f^{13}	100.8	4194	4220
71	Lu	$[Xe]4f^{14}5d^16s^2$	f^{14}	100.1	3887	4360

Table 1.1 Electron configurations of the lanthanoid atoms and their tripositive ions.

[†] *metal cation showing six-fold coordination (Shannon 1976)*

As a generalisation, $IP_4 \sim 2(IP_3) \sim 4(IP_2) \sim 8(IP_1)$ and $IP_4 > (IP_1+IP_2+IP_3)$

[*] *sum of first three ionisation potentials (Bernal et al 2004)*

[**] *fourth ionisation potential (Bernal et al 2004)*

[Xe] represents a xenon atomic core i.e. $[1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^{10}\,4p^6\,5s^2\,4d^{10}\,5p^6]$
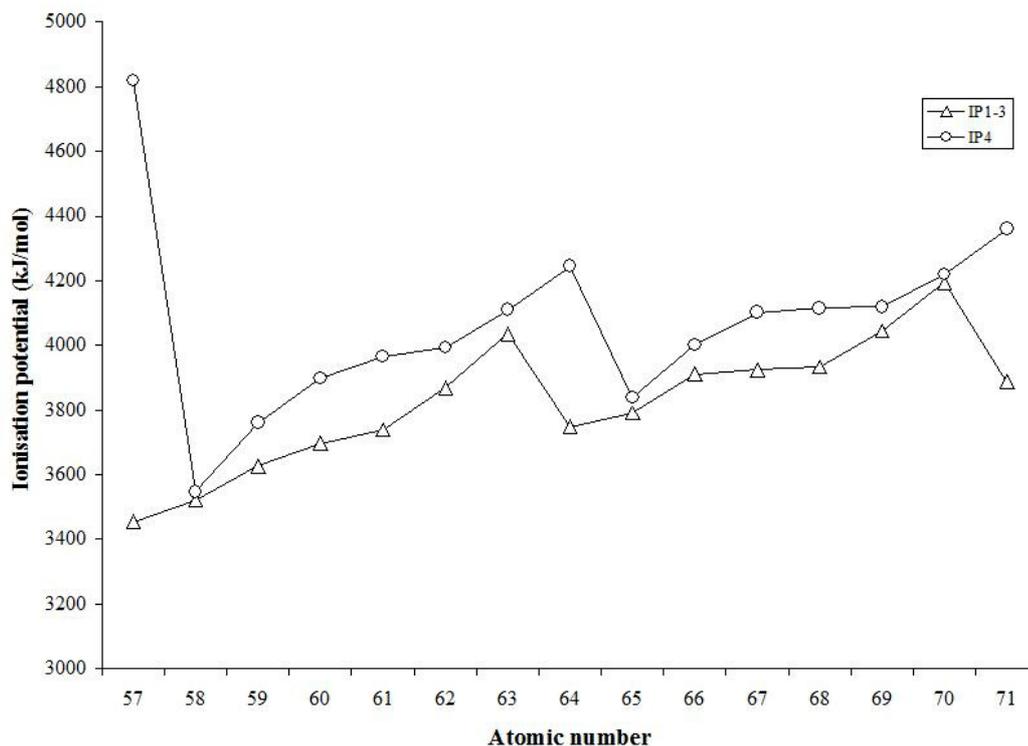
Figure 1.1 ΣIP$_{1-3}$ and IP$_4$ for the lanthanoids (Bernal et al 2004).

Table 1.1 shows that the sum of the first three ionisation potentials for the lanthanoids is fairly consistent across the series, indicating the +3 state to be a common one. Indeed, this state is the preferred one under ambient conditions for most elements in the series, other than those with a relatively low second or fourth ionisation potential. Cerium, praseodymium and terbium all exhibit the +4 state, as well as displaying oxides with mixed +3/+4 valencies such as Pr_6O_{11} and Tb_4O_7. Cerium is the only lanthanoid to be stable in the +4 oxidation state in aqueous solution. The only binary cerium IV compounds known are CeF_4 and CeO_2. There are several stable complexes containing Ce^{4+}, for example $(NH_4)_2[Ce(NO_3)_6]$, in which the nitrate ion acts as a bidentate ligand, the co-ordination of the Ce^{4+} being icosahedral. Only europium shows a marked tendency for lower oxidation states, for example Eu^{2+} exists in EuO and EuC_2O_4, although neodymium, samarium and ytterbium also show some tendency for this oxidation state. Table 1.2 below lists the oxidation states attainable by the lanthanoids and their corresponding electron configurations.

Element	Oxidation state	Electron configuration
La	+3	[Xe] noble gas
Ce	+3	$[Xe]4f^1$
	+4	[Xe] noble gas
Pr	+3	$[Xe]4f^2$
	+4	$[Xe]4f^1$
Nd	+2	$[Xe]4f^4$
	+3	$[Xe]4f^3$
Pm	+3	$[Xe]4f^4$
Sm	+2	$[Xe]4f^6$
	+3	$[Xe]4f^5$
Eu	+2	$[Xe]4f^7$ half shell
	+3	$[Xe]4f^6$
Gd	+3	$[Xe]4f^7$ half shell
Tb	+3	$[Xe]4f^8$
	+4	$[Xe]4f^7$ half shell
Dy	+3	$[Xe]4f^9$
Ho	+3	$[Xe]4f^{10}$
Er	+3	$[Xe]4f^{11}$
Tm	+3	$[Xe]4f^{12}$
Yb	+2	$[Xe]4f^{14}$ full shell
	+3	$[Xe]4f^{13}$
Lu	+3	$[Xe]4f^{14}$ full shell

Table 1.2 Electron configurations of the lanthanoids.

1.3 THE LANTHANIDE CONTRACTION

The elements in the first row of the f block exhibit a decrease in atomic radius from lanthanum, Z=57 to lutetium, Z=71. Because of this phenomenon, termed the *lanthanide contraction*, vertically-adjacent elements in the 2nd and 3rd rows of the d block, which appear before and after the lanthanoids, have very similar atomic radii even though they contain very different numbers of electrons. For example, the atomic radii of zirconium and hafnium are 1.60Å and 1.59Å respectively; for silver and gold the figures are both 1.44Å. With a significant increase in atomic weight and little or no change in atomic radius there is an associated increase in density. For example, gold has approximately twice the density of silver. Moving from left to right across the 1st

row of the f block there is a steady decrease in atomic radius with increasing atomic number. This contraction is also shown in the radii of the tripositive ions, illustrated in figure 1.2. This decrease in ion size is accompanied by the filling of the 4f orbitals.

Before the electronic structures of the lanthanoids were elucidated by spectroscopy, they could only be assumed. It was correctly believed that the electronic structure of the lanthanum atom was $[Xe]5d^1 6s^2$. It was therefore easy to explain the existence of the +3 oxidation state by the loss of the three outer electrons. Assuming that the $5d^1 6s^2$ electrons were retained across the series of atoms from $[Xe]5d^1 6s^2$ to $[Xe]4f^{14}5d^1 6s^2$ and that moving across the lanthanoids corresponded to the filling of the 4f shell, the predominance of the +3 oxidation state could be explained as each atom could lose the $5d^1 6s^2$ electrons to form the tripositive ion. However, spectroscopy has revealed that the atoms and ions do not all have the $[Xe]4f^n 5d^1 6s^2$ and $[Xe]4f^n$ structures respectively. The removal of electrons from a lanthanoid atom proceeds in the manner of first the outer 6s electrons, secondly the outer 5d electrons and thirdly the 4f electrons. Because of their greater affinity for the nucleus and hence the shorter radial extension of their atomic orbitals, the 4f electrons are termed *inner* or *core* electrons.

In a multi-electron atom, the distance an electron exists from the nucleus is determined by both the shell in which it lies and the nuclear charge. Increasing nuclear charge causes a shrinking of the atomic radius. However, this shrinkage is offset to some degree by the presence of the inner electrons. This is due to a shielding effect; inner electrons shield the outer electrons from the nucleus. Therefore, rather than experience the full nuclear charge, Z, the outer electrons experience an effective nuclear charge, Z_{eff}. The shielding effect of occupied atomic orbitals decreases in the order s > p > d > f. Because of their limited radial extension and their highly angular shapes, the 4f atomic orbitals have a poor shielding effect and the shielding gained on adding electrons to the 4f orbitals on crossing the lanthanoid series fails to compensate for the increasing nuclear charge. For the lanthanoids, Z_{eff} is seen to increase steadily with increasing atomic number, causing the electrons to be drawn in towards the nucleus. Consequently there is a steady and almost linear decrease in atomic radius with increasing atomic number. This contraction is also shown in the radii of the tripositive ions, shown in figure 1.2.
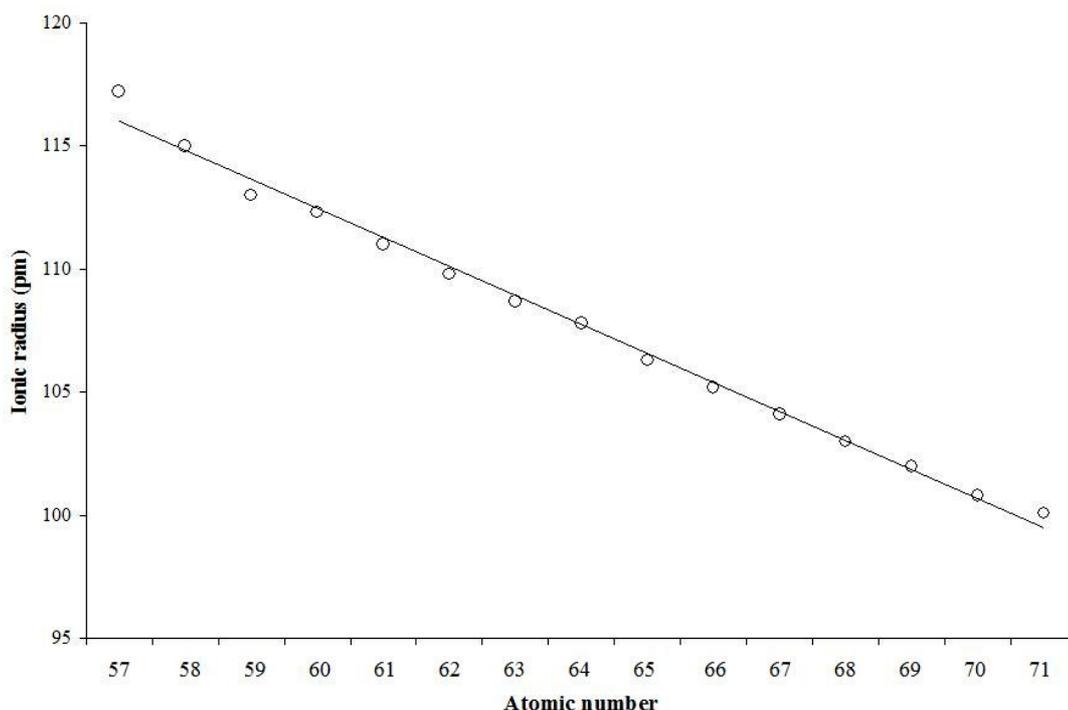
Figure 1.2 Ionic radii for the tripositive ions Z=57 to 71 (Shannon 1999).

This poor shielding ability of the 4f electrons is believed to be the major contributor to the lanthanide contraction, although studies reveal about 10% of the contraction is due to relativistic effects (Pyykkö and Descleaux 1979). In heavy atoms such as the lanthanoids, the effects of special relativity become significant for high-speed electrons and result in both a contraction of the radial extension of atomic orbitals and an increase in the rest mass of electrons. Consequently there is a decrease in the atomic radius. Other notable examples of chemical relativistic effects are the physical state of mercury at ambient temperature and the colour of gold. Mercury is known to exist as the monoatomic species Hg in the gaseous state. The contraction of the valence electron shell means it does not play a significant role in bonding and so the atoms in the liquid are held together by weak Van der Waals forces alone. With gold, the contraction of the 6s orbital means the $5d \rightarrow 6s$ energy transition is shifted from the ultra-violet into the visible part of the electromagnetic spectrum. The wavelength of light concerned is in the blue region of the spectrum, resulting in the metal having its distinctive yellow colour (Norrby 1991).

1.3.1 The lanthanide contraction illustrated in unit cell parameters

Because of the existence of the lanthanide contraction the possibility arises that the unit cell parameters for particular series of compounds might also follow a contraction. For example, if a particular lanthanoid compound exhibits cubic symmetry, then the rest of the lanthanoids when present in the same type of compound might also exhibit the same symmetry. Furthermore, a plot of the unit cell parameter against atomic number might show a trend similar to that of the lanthanide contraction. There are many references citing cases of series of lanthanoid compounds exhibiting a common structure (Siddiqui and Hoppe 1975), (Feldner and Hoppe 1980), (Urland *et al* 1980), (Aléone and Pouzet 1968). Aléone and Pouzet consider the series of compounds Rb_2NaLnF_6 and Cs_2NaLnF_6, where Ln is a lanthanoid, and state that all are cubic with the perovskite structure and of space group Fm3m. Unit cell data for the series of cubic structures Rb_2NaLnF_6 is given in table 1.3 and illustrated in figure 1.3. It is clear that the trend in the cell size across the series is similar to that of the tripositive ionic radii. Data for the series of tetragonal structures $LiLnF_4$ is given in table 1.4 and illustrated in figure 1.4. ICDD is the International Centre for Diffraction Data.

Z	Element	ICDD ref	Cell a (Å)	Crystal system	Space group
62	Sm	21-1041	8.988	Cubic	*Fm3m*
65	Tb	21-1042	8.921	Cubic	*Fm3m*
67	Ho	21-1040	8.881	Cubic	*Fm3m*
68	Er	20-1384	8.867	Cubic	*Fm3m*
70	Yb	21-1043	8.816	Cubic	*Fm3m*

Table 1.3 Unit cell parameters for the cubic series Rb_2NaLnF_6 (ICDD 1995).
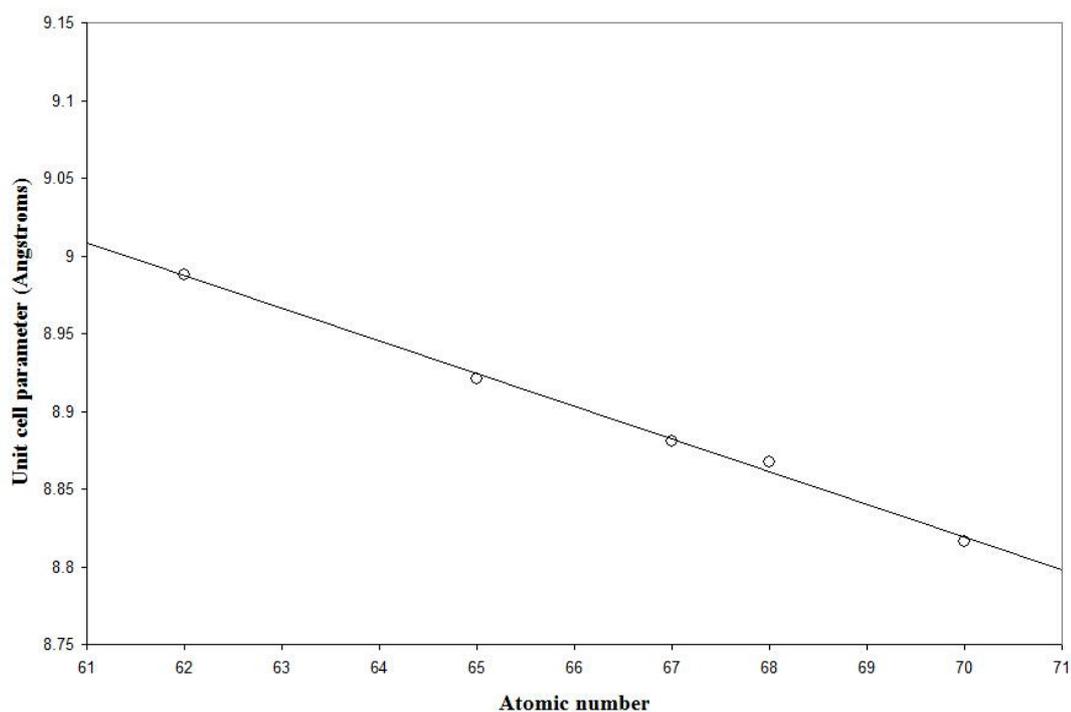
Figure 1.3 Atomic number versus unit cell parameter for the cubic series Rb$_2$NaLnF$_6$

(ICDD 1995).

Z	Element	ICDD ref	Cell a (Å)	Cell c (Å)	Crystal System	Space group
63	Eu	27-0292	5.21	11.02	Tetragonal	$I4_1/a$
64	Gd	27-1236	5.21	11.00	Tetragonal	$I4_1/a$
65	Tb	27-1262	5.19	10.89	Tetragonal	$I4_1/a$
66	Dy	27-1233	5.19	10.81	Tetragonal	$I4_1/a$
67	Ho	27-1243	5.16	10.75	Tetragonal	$I4_1/a$
68	Er	27-1235	5.16	10.70	Tetragonal	$I4_1/a$
69	Tm	27-1265	5.15	10.64	Tetragonal	$I4_1/a$
70	Yb	23-0371	5.13	10.58	Tetragonal	$I4_1/a$
71	Lu	27-1251	5.13	10.53	Tetragonal	$I4_1/a$

Table 1.4 Unit cell parameters for the tetragonal series LiLnF$_4$ (ICDD 1995).
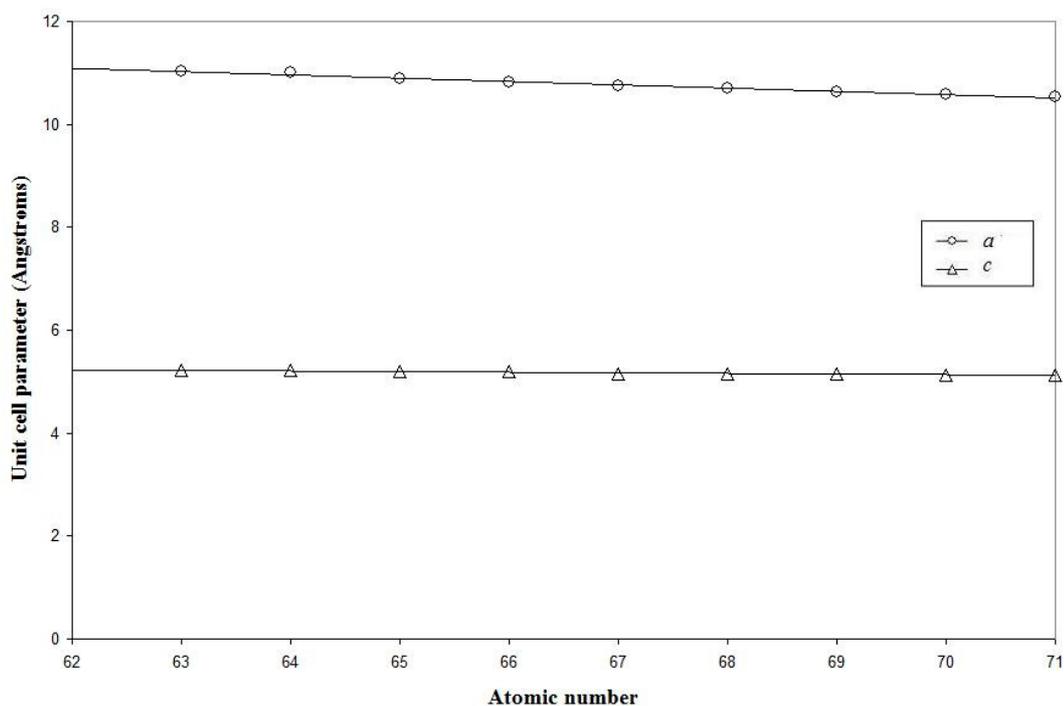
Figure 1.4 Atomic number versus unit cell parameters for the tetragonal series LiLnF₄ (ICDD 1995).

Because of this trend across series of lanthanoid compounds, it is often a good starting point when considering an unknown structure to look at the structures of the same compounds of the adjacent metals. In many cases the cell type and space group will be the same. Furthermore, the unit cell parameters may be the same, subject to an adjustment according to the lanthanide contraction. In such a case, the atom positions are also likely to be the same. However, a single cell type is not generally representative of any one series of lanthanoids. There are series of compounds where the shrinking co-ordination sphere of the metal induces a change in cell type. For example, with the lanthanoid sesquioxides there is a shift from the 7-fold co-ordination of a hexagonal structure, to the 6-fold co-ordination of a cubic structure. In such a series a break would be seen in the plot of unit cell parameters; a pair of lines corresponding to the values for *a* and *c* in the hexagonal cell would switch to a single line corresponding to the single cubic cell parameter. For both cell types the plots would still follow the downward trend of the lanthanide contraction.

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1.4 LANTHANOID COMPOUNDS

1.4.1 Overview

The crystal structure of the simple compounds such as the sesquioxides and halides exhibit high co-ordination numbers due to the large sizes of the tripositive lanthanoid ions. The sesquioxides are the most stable oxides, except for those of cerium, praseodymium and terbium, whose oxides contain the metal wholly (cerium) or partly (praseodymium and terbium) in the +4 oxidation state. At ambient temperature the sesquioxides of the lighter lanthanoids exhibit hexagonal symmetry. Heavier sesquioxides exhibit cubic symmetry. The monoxide of europium is known but there is doubt as to the phases of other low-oxygen species. Higher oxides exist, notably that of cerium. Ceric oxide, CeO_2, has the fluorite structure (as do PrO_2 and TbO_2) but a range of phases is known to exist, with some intermediate between Ce_2O_3 and CeO_2, for example $Ce_{32}O_{58}$, $Ce_{32}O_{57}$ and $Ce_{18}O_{31}$. The compound Pr_6O_{11} exists as a mixed phase of the +3 and +4 oxides in the ratio 1:4 and may be converted to Pr_2O_3 with hydrogen at high temperature. As with cerium there exists a range of phases between the sesquioxide and the dioxide. The intermediate oxide Ln_7O_{12} is also known for lanthanum, cerium, praseodymium and terbium. The general property of many rare earth oxides is that they have defect lattices in which some O^{2-} vacancies in the LnO_2 fluorite structure are compensated for by the presence of Ln^{3+} ions.

The sulphides, selenides and tellurides exhibit the compounds LnS, Ln_3S_4, Ln_2S_3 and LnS_2 but there are many non-stoichiometric compounds in addition to these. The interest in these compounds lies in their semi-conducting properties.

The hydroxide ion has a similar radius to the fluoride ion and consequently, for the light lanthanoid trifluorides and hydroxides, the same crystal structure is exhibited, that of tysonite, LnF_3, with each lanthanoid co-ordinated to 9 fluorides anions. For the trichlorides of the elements lanthanum to gadolinium the UCl_3 structure is adopted with nine-fold co-ordination around a trigonal prism with 3 chlorides against the three vertical faces. Terbium trichloride adopts the eight-fold co-ordination $PuBr_3$ structure and for the metals dysprosium to lutetium the six-fold co-ordination of $FeCl_3$ is evident.

The tribromides adopt the same structures as the trichlorides. The triiodides adopt the PuBr$_3$ structure for lanthanum to neodymium and the FeCl$_3$ structure for samarium to lutetium. Lower halides are known; the difluorides of samarium, europium and ytterbium exhibit the fluorite structure. The difluorides of thulium and ytterbium exhibit the structure of CaI$_2$. The dichlorides of neodymium, samarium, europium, dysprosium and ytterbium are prepared by the reduction of the trichloride with the lanthanoid. The dibromides of samarium, europium, thulium and ytterbium and the diiodides of lanthanum, cerium, praseodymium, neodymium and gadolinium are prepared in a similar way. Diiodides are also obtained by thermal decomposition of the triodides. Tetrafluorides of cerium, praseodymium and terbium are known, having the UF$_4$ structure of a square anti-prism. Attempts to make other tetrafluorides have been unsuccessful but the complexes Cs$_3$[NdF$_7$] and Cs$_3$[DyF$_7$] have been made by fluorination of a mixture of caesium chloride and the lanthanoid trichloride. As a general rule, for all classes of compounds there is a trend of decreasing co-ordination number with decreasing ionic radius.

1.4.2 The lanthanoid sesquioxides

Historically the lanthanoid sesquioxides have been extensively studied, the first notable publication being in 1925 (Goldschmidt *et al* 1925). This study first highlighted the three structural types, A, B and C. Their crystallographic forms and polymorphism have been reviewed on a number of occasions (Brauer 1968), (Haire and Eyring 1994), (Adachi and Imanaka 1998), (Zinkevich 2007). Below 2000°C the sesquioxides exist in three crystal systems i.e. the cubic C-type, the monoclinic B-type and the hexagonal A-type. With increasing temperature the stability of the structures is generalised by the order C → B → A, although not every oxide will exhibit all phases; this general transition is typical of the middle members of the group. Under ambient conditions the A-type oxide is preferred for lanthanum to promethium, although it may exist in combination with the C-type. C-type cerium sesquioxide is actually a non-stoichiometric oxide showing a range of oxygen content, but designated Ce$_2$O$_3$. Both C and B-type oxides exist for samarium, europium and gadolinium. The C-type is stable under ambient conditions from samarium onwards and for the heavier metals of the series this phase is preferred, although it may exist in combination with the B-type

oxide, the fraction of B-type falling with increasing weight of the metal. For lutetium the C-type oxide is the only phase known, as there is a direct transition to the molten state at approximately 2400°C.

Above 2000°C an additional two types, denoted by H and X, are present (Föex and Traverse 1966). These are believed to be modifications of the hexagonal and cubic phases, respectively (Aldebert and Traverse 1979). Only a very few lanthanoid sesquioxides exhibit all five phases (promethium, samarium and europium). A phase diagram showing all five modifications is given in figure 1.5.
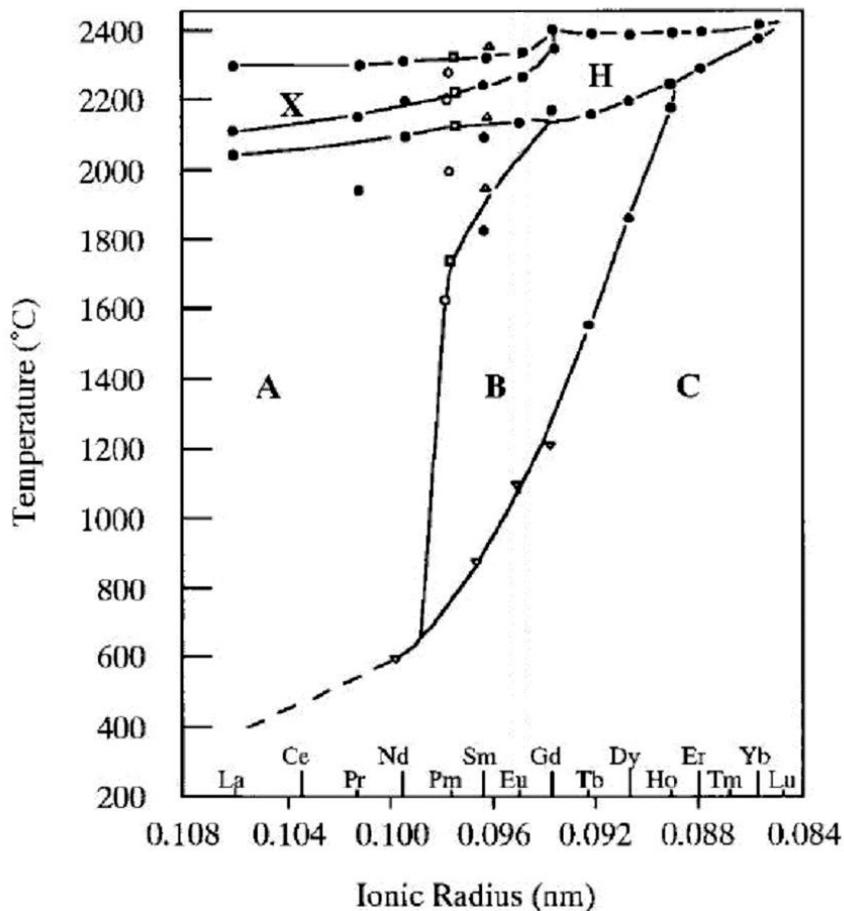
Figure 1.5 Phase diagram for the lanthanoid sesquioxides (Föex and Traverse 1966).

The accepted phase diagram for these 5 polymorphs was constructed from two data sources (Warshaw and Roy 1961), (Föex and Traverse 1966). The diagram shows the three structure types that exist at ambient temperature. For the lighter oxides, the ambient phase is hexagonal and this phase exists until the exotic high temperature H-

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and X-types are reached at over 2000°C. For the intermediate oxides, the ambient phase is cubic. On heating, there is a transition to the monoclinic phase before the H and X-types are reached. After holmium sesquioxide, the only phase is cubic until the H phase is reached.

The structures of the three main phases are well known. The A-type exists in space group P-$3m$1 with one formula unit per unit cell. The metal atoms occupy the 4f sites of the space group. 4 of the oxygen atoms occupy the same sites; the remaining 2 oxygen atoms occupy the 2a sites. The metal atoms are in seven-fold co-ordination to oxygen with four oxygen atoms closer than the other three.
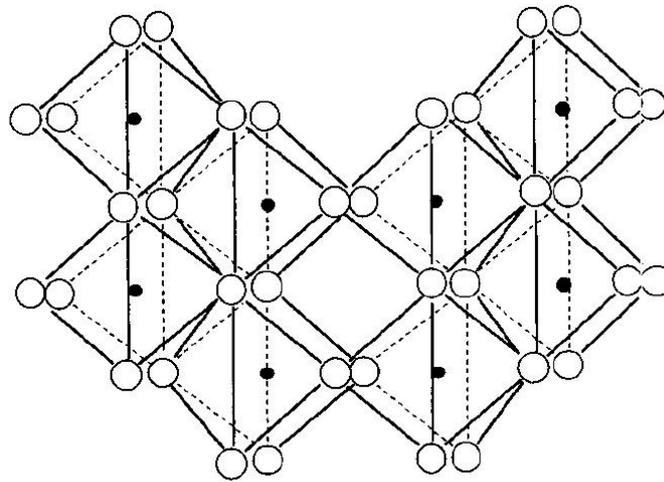
Figure 1.6 A-type (hexagonal) Ln_2O_3 (where Ln represents any lanthanoid). Solid dots represent metal centres (Eyring 1979).

The B phase, a distortion of the A-type, exists in space group $C2/m$ with six formula units per unit cell. All 12 metal atoms occupy the 4i sites of this space group. 16 oxygen atoms also occupy the 4i sites, with a further 2 oxygens occupying the 2b sites. The metal atoms in this phase are six-fold and seven-fold co-ordinated to oxygen.
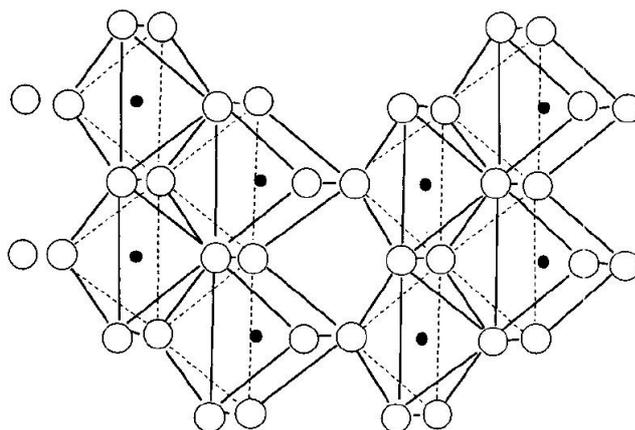
Figure 1.7 B-type (monoclinic) Ln$_2$O (Eyring 1979).

The C-type has the bixbyite structure in space group *Ia*-3, bixbyite having its most common form as Mn$_2$O$_3$. The unit cell contains 32 metal atoms (on the 8b and 24d sites) and 48 oxygen atoms (occupying all 48e sites). The structure is effectively a fluorite lattice with a quarter of the oxygen sites vacant. In this structure the metal atoms are six-fold co-ordinated to oxygen.
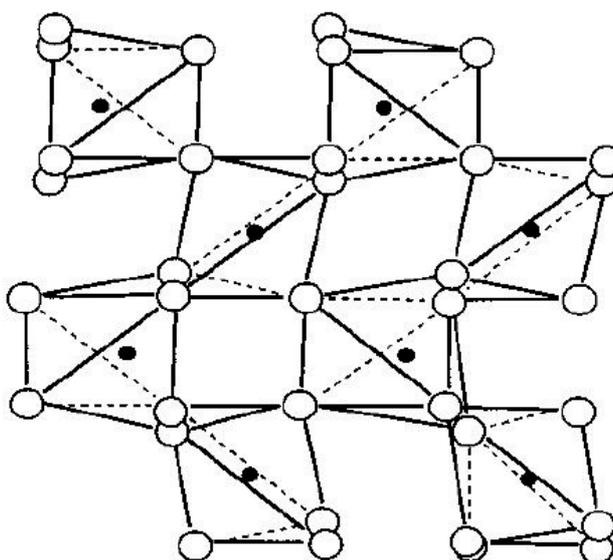
Figure 1.8 C-type (cubic) Ln$_2$O$_3$ (Eyring 1979).

1.4.3 The praseodymium-oxygen system

When the ratio of oxygen to metal is variable, the praseodymium-oxygen system shows a number of discrete phases. In fact, of all the rare earth oxides, the praseodymium-oxygen system is the most complex. In addition to the green-coloured sesquioxide there are six well-established and well-studied oxides. The majority of work on the praseodymium-oxygen system comes from Eyring and co-workers in a series of papers, the most significant of which (Hyde *et al* 1965) established the phase diagram in figure 1.9. Here is confirmed the existence of the ι ($x = 1.71$), ξ ($x = 1.78$), ε ($x = 1.80$) and β ($x = 1.83$) phases, together with two wide-ranging non-stoichiometric phases. These are the face-centred α phase, with $2.00 \geq x \geq 1.72$ and the body-centred σ phase, with $1.7 \geq x \geq 1.6$. Observed for the first time is the δ ($x = 1.816$) phase. It was also established that the discrete monophasic species were members of an incomplete homologous series corresponding to the formula Pr_nO_{2n-2} for values of $n = 4, 7, 9, 10, 11, 12$ and ∞. These phases are listed in table 1.5.

n	Formula	phase	*x* in PrO$_x$	Cell	Existence
4	Pr_2O_3	ϕ	1.5	B-type BCC	<275°C
		θ	1.5	A-type Hexagonal	>900°C
7	Pr_7O_{12}	ι	1.714	Rhombohedral	500-1000°C
9	Pr_9O_{16}	ξ	1.778	Rhombohedral	450-600°C
10	Pr_5O_9	ε	1.8	FCC	300-500°C
11	$Pr_{11}O_{20}$	δ	1.818	FCC	375-475°C
12	Pr_6O_{11}	β	1.833	FCC	275 to 475°C
∞	PrO_2	α	2	FCC	>500°C

Table 1.5 Discrete phases in the praseodymium-oxygen system.

Aside from the sesquioxide Pr_2O_3, the red-black material Pr_6O_{11}, sometimes referred to as the *air-ignited* oxide, is the only other oxide stable at ambient temperature. On heating the pale green sesquioxide it is the first oxide to be created. Other than PrO_2, this material contains the greatest ratio of oxygen to metal. Further heating gradually reduces this ratio through the phases $Pr_{11}O_{20}$, Pr_5O_9, Pr_9O_{16}, Pr_7O_{12} and eventually back to Pr_2O_3. The various known phases are shown in figure 1.9.
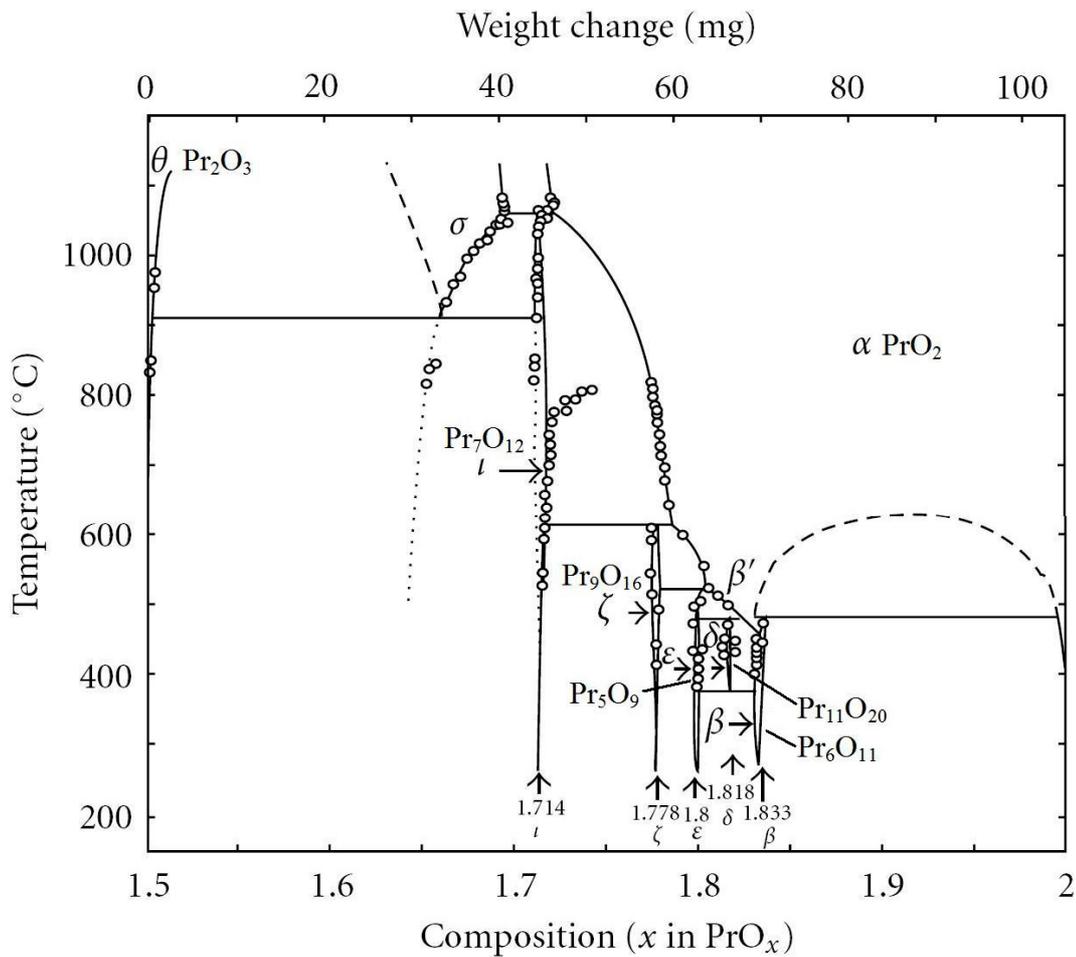
Figure 1.9 Phase diagram for the praseodymium-oxygen system (Hyde at al 1965).

It has been claimed that praseodymium may exhibit the +5 oxidation state (Prandtl 1925) and that the air-ignited oxide has the formula $2Pr_2O_3.Pr_2O_5$. However, later work (Marsh 1946) shows that the highest oxidation state attainable by praseodymium is +4. This is supported by other work (Zintl and Morawietz 1940) and shows Pr_6O_{11} as the double oxide $4PrO_2.Pr_2O_3$.

1.5 AIMS OF THIS WORK

1.5.1 Determination of structures resulting from temperature-induced phase transitions

Investigation and characterisation of the structural changes in ceramic materials at high temperature are particularly important. For example, europium sesquioxide is used within nuclear reactor control rods because of its neutron absorbing ability, while ytterbium sesquioxide has been proposed as a component within thermophotovoltaic energy conversion devices (Krishna 1999), (Durisch and Bitnar 2010). Both applications cause structure changes in the oxides and hence an understanding of these changes is important to their operation.

Although the series has been extensively studied, there are a number of omissions in the published work. Not all structures indicated by the phase diagram have been synthesised and their structures recorded. Some of these omissions are addressed in this thesis. Two databases were used as the main source of reference material in this work. The first is the Daresbury ICSD database (ICSD website), existing until January 2013 but now commissioned by the RSC (Royal Society of Chemistry). The second is the ICDD Powder Diffraction File PDF-2 (ICDD 1995).

Of particular interest to this study was the unpublished structure of the B-type phase of Gd_2O_3. Within the Daresbury database there are three distinct structural types of Gd_2O_3, all of which are cubic. They are $a = 10.80$Å, space group $Ia3$ (Saiki *et al* 1984), $a = 10.81$Å, space group $I213$ (Zachariasen 1928) and $a = 5.21$Å, space group Fm3m (Kashaev *et al* 1975). The PDF-2 database lists 5 entries for Gd_2O_3, two of which are cubic, space group $Ia3$, 1 is hexagonal (Föex 1966) and 2 are monoclinic, space group $C2/m$ (Guentert and Mozzi 1958), (Grier and McCarthy 1991).

The phase diagram for the sesquioxides implies that there are no monoclinic phases existing at ambient temperature. Goldschmidt *et al* were unable to identify the cell for the B-type oxide, stating it to be pseudotrigonal, orthorhombic or monoclinic. The first publication of the monoclinic cell was over thirty years later (Douglass and Staritsky 1956) with the atom positions established the following year (Cromer 1957).

Historically there have been a number of studies on B-type Gd_2O_3 (Guentert and Mozzi 1958), (Grier and McCarthy 1991). Although none of these studies published a description of the unit cell, both concur that the system is analogous to that of B-type Sm_2O_3. Furthermore, and contrary to the phase diagram, Guentert and Mozzi remark that their B form was stable at ambient temperatures. The known structures of both Eu_2O_3 and Sm_2O_3, both having similar unit cell parameters and the same space group, would therefore be a useful starting point for the determination of the structure of monoclinic Gd_2O_3 and for determining if this high temperature modification could be retained on cooling.

It is interesting to note that there is a general lack of entries in the Daresbury database for the B-types. The phase diagram indicates that for increasing atomic number of the lanthanoid, an increasingly high temperature is required to convert the C-type to the B-type. However, the diagram also indicates that after Ho_2O_3 the C-type converts either to the H-type before melting, or just melts, and that no B-type exists. It is only quite recently that heavy (Ho_2O_3 and above) monoclinic sesquioxides have been reported. Just prior to the construction of the sesquioxide phase diagram it had been stated that no monoclinic phases existed beyond Dy_2O_3 (Warshaw and Roy 1961). The ICSD database reports monoclinic structures for Sm_2O_3, Eu_2O_3 and Tb_2O_3, together with a recent entry for Er_2O_3 (Wontcheu and Schleid 2008). There is also a recent study reporting the structures of a number of A and B-types across the series, although these have been obtained theoretically (Wu *et al* 2007). Considering the report of the existence of B-type Er_2O_3 (contrary to the phase diagram), it was decided to investigate the possibility of there being a B-type cell for the only monoclinic species without any entry whatsoever in the ICSD database, namely ytterbium sesquioxide. There are reports of these heavy atom B-type oxides being obtained via temperature *and* pressure, including those of ytterbia and lutetia (Hoekstra and Gingerich 1964), (Hoekstra 1966). The use of inductively coupled radio frequency plasma spraying to create a residual monoclinic phase of lutetia within an otherwise cubic sample has also been reported (Sun *et al* 2007). However, my work was concerned only with structural conversions obtained via increased temperature. A recent high-pressure study (Meyer *et al* 1995) has shown the structure of monoclinic Yb_2O_3. A study at ambient pressure (Guo, Harvey *et al* 2007) has shown the creation of nanoparticles of B-type Dy, Ho, Er, Tm

and Yb sesquioxides by a method of flame synthesis. Another study (Guo *et al* 2007) has shown the creation of B-type Er_2O_3 under pressure, which could be quenched to ambient conditions. These references imply that there are modifications to be made to the phase diagram i.e. the lines drawn thereupon are not absolute. The inference is that it might be possible to create monoclinic ytterbia in the bulk material at high temperature and retain it to ambient temperature.

1.5.2 Kinetic studies

There has been considerable work done on the kinetics of the $C \rightarrow B$ transition of the intermediate oxides (Sm_2O_3, Eu_2O_3 and Gd_2O_3). There are two notable references (Stecura 1966), (Ainscough *et al* 1975), but to date no kinetic work has been carried out on the heavier oxides. In addition, there are gaps in work on the kinetics of the $C \leftrightarrow A$ transitions for the lighter oxides. Although Stecura did look at the kinetics for La_2O_3 and Nd_2O_3, there has been no work done on Ce_2O_3 (presumably because of the lack of a pure sesquioxide) and Pr_2O_3. All kinetic studies have involved the raising of a sample to a number of temperatures and at each temperature noting the degree of conversion with time. Using XRPD data, Stecura measured this variation by noting the change in the integrated intensity of the 222 Bragg reflection from the low temperature modification. Ainscough measured it by comparing the patterns to a series of standards containing both cubic and monoclinic phases in varying proportions.

Although their respective structures are well documented, there is no kinetic data for the $C \rightarrow A$ phase transition in Pr_2O_3. It was therefore decided to perform a kinetic study of this phase change by taking powder diffraction patterns in situ.

Further, there is no data for the $\theta \rightarrow \beta$ or the higher temperature phase transitions in the Pr-O system, or the $C \rightarrow B$ phase transition in Tb_2O_3. It was decided to investigate the former by a combination of DSC and XRPD and the latter by DSC alone.

1.5.3 Investigating and redrawing phase diagrams

Finally, the above results would be compared to the current phase diagrams for the oxides and an attempt would be made at redrawing them.

2 X-RAY DIFFRACTION

2.1 THEORY

2.1.1 The Bragg Construction

In 1912 Walter Friedrich and Paul Knipping, working under Max von Laue, demonstrated the diffraction of X-rays, using a single crystal of copper sulphate for a grating. Laue was subsequently awarded the Nobel Prize for demonstrating the both wave-like nature of X-rays and the periodic internal structure of a crystal. The explanation of these results in terms of crystal structure and the behaviour of X-rays inside the crystal was carried out by W.H and W.L. Bragg in 1913 for which they jointly won the Nobel Prize. Since then X-ray crystallography has become a powerful and well-established tool for structure determination in the solid state.

Laue's postulate that a crystal consisted of regularly spaced particles was confirmed by this famous experiment. A photographic plate placed beyond the sample showed a series of dark spots where X-rays had fallen after reflection from the crystal. He proposed that different spots on the photograph were caused by different wavelengths of X-rays. The Braggs interpreted these spots quite differently, explaining them as showing diffraction occurring only in certain definite directions from the three-dimensional periodic structure of the crystal. Rather than the slits of a diffraction grating, the spacing now corresponded to the perpendicular distance between adjacent parallel planes of atoms in the crystal. In certain directions, the wavelets propagating from successive planes would constructively interfere and produce a dark spot, or Bragg peak.

The Braggs considered the crystal as a series of parallel planes separated by a distance, d, which, for the purpose of the construction, act like mirrors. This is illustrated in figure 2.1. X-rays arriving from the left are incident on the parallel crystal planes at an angle θ and leave the crystal at the same angle. The path difference between the top and bottom waves is a multiple of the wavelength, λ.
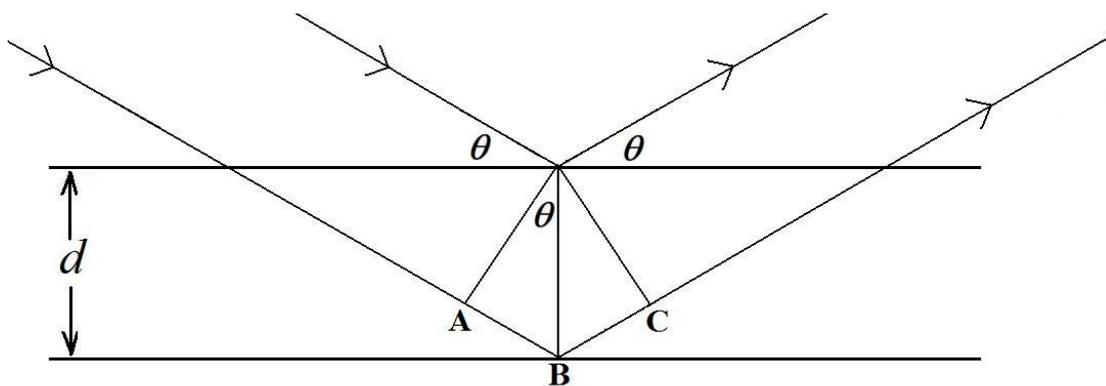
Figure 2.1 The Bragg Construction.

From figure 2.1

$$AB + BC = n\lambda \tag{2.1}$$

Therefore:

$$\sin\theta = \frac{n\lambda}{2d} \tag{2.2}$$

Rearranging gives the Bragg equation:

$$n\lambda = 2d\sin\theta \tag{2.3}$$

where n is an integer corresponding to the order of the diffracted beam.

The Bragg equation describes the condition for constructive interference from any set of parallel planes of the crystal, separated by a distance d.

2.1.2 Describing crystal planes and reflections

A crystal is a repeat structure in three dimensions and the basic building block from which it is constructed is called the unit cell. To illustrate this, figure 2.2 shows a unit cell. The 3 side lengths in 3-dimensional space are termed a, b and c. The 3 interaxial angles are termed α, β and γ.
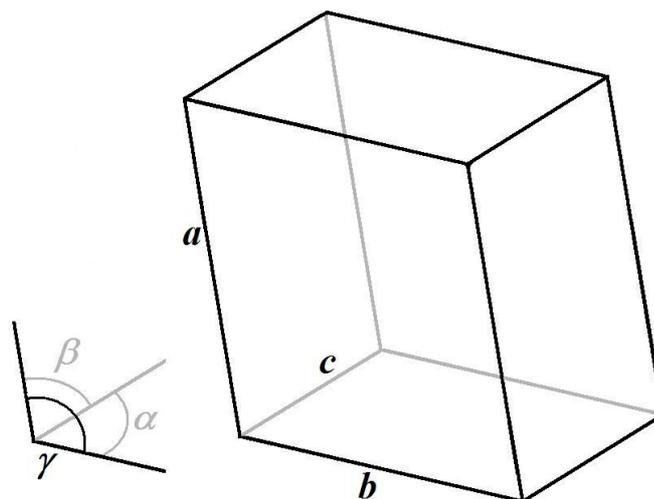
Figure 2.2 A unit cell. Cell edges are represented by a, b and c, interaxial angles by α, β and γ.

In the simplest terms there are seven types of cell, each displaying different symmetries. The highest symmetry is expressed by the cubic cell, which has one parameter, namely the length of its edge. The lowest symmetry is shown by the triclinic cell, with three different cell edges and three different interaxial angles. The seven crystal systems are detailed in table 2.1, along with their associated degrees of freedom and the restrictions placed on the unit cell parameters.

Crystal system	Degrees of freedom	Restrictions
Cubic	1	$a = b = c$; $\alpha = \beta = \gamma = 90°$
Tetragonal	2	$a = b \neq c$; $\alpha = \beta = \gamma = 90°$
Hexagonal	2	$a = b \neq c$; $\alpha = \beta = 90°$; $\gamma = 120°$
Trigonal	2	$a = b = c$; $\alpha = \beta = \gamma \neq 90°$
Orthorhombic	3	$a \neq b \neq c$; $\alpha = \beta = \gamma = 90°$
Monoclinic	4	$a \neq b \neq c$; $\alpha = \gamma = 90° \neq \beta$
Triclinic	6	$a \neq b \neq c$; $\alpha \neq \beta \neq \gamma \neq 90°$

Table 2.1 The seven crystal systems.

The seven crystal systems represent the building blocks of a crystal at its most basic level. If we consider any of these cells to contain a single repeat unit i.e. only one point of symmetry (at each of its 8 vertices) then we obtain the 7 primitive cells. However, when translational symmetry is also taken into consideration it is found that there are

actually 14 cell types, called the Bravais Lattices (or Space Lattices). These take into account all possible combinations of cell-centered and face-centered symmetry points. The 14 Bravais Lattices are illustrated in figure 2.3.
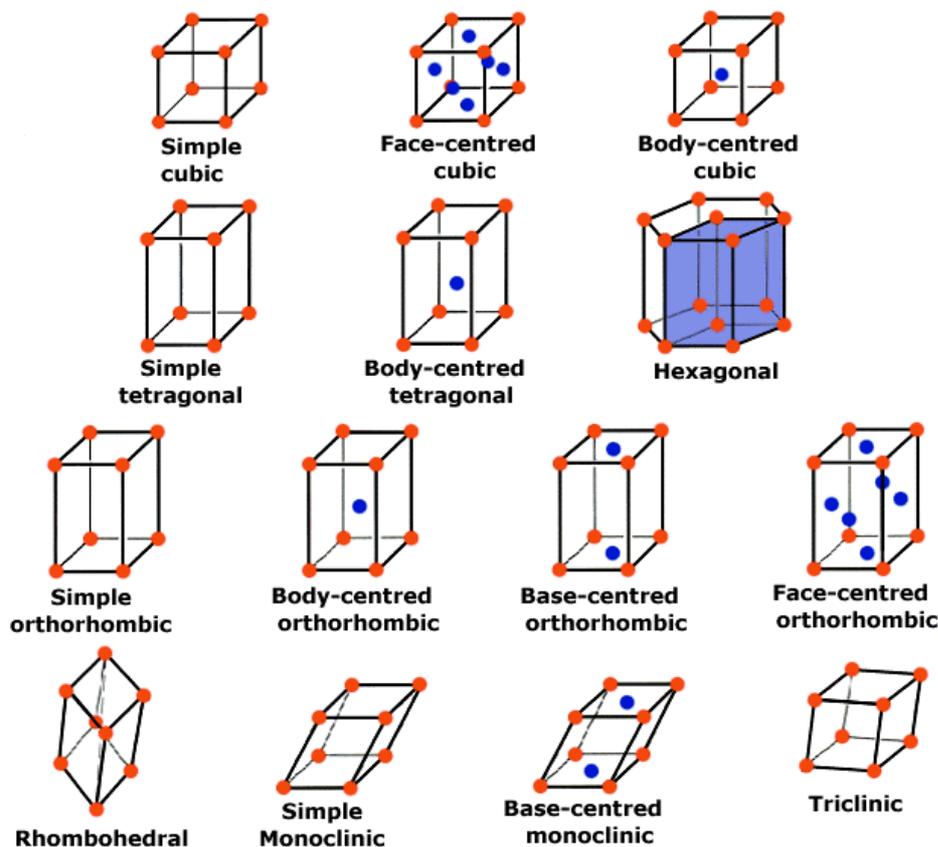
Figure 2.3 The 14 Bravais Lattices. Image from
http://www.seas.upenn.edu/~chem101/sschem/solidstatechem.html

A crystal lattice is a repeat structure in 3-dimensional space with each point in the lattice representing a physical unit. For example, the primitive cubic cell has one repeat unit at each vertex. This unit may be as simple as a single atom. It might be a group of atoms or an organic molecule. Since each of these 8 points is shared amongst 8 adjoining unit cells, there is actually only one repeat unit per cell. The body-centred unit cell has the one repeat unit by virtue of its 8 vertices and another repeat unit at the body centre, making a total of 2 in the unit cell. The face-centred unit cell again has the one repeat unit of the primitive cell plus another 3 by virtue of its face-centred units, making a total of 4 in the unit cell.

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2.1.3 Crystal planes

Any set of parallel planes within a crystal lattice can be described by 3 numbers, called the Miller indices of the planes. The numbers represent the number of intercepts on each of the 3 spatial axes within a single unit cell. Figure 2.4 illustrates this concept.
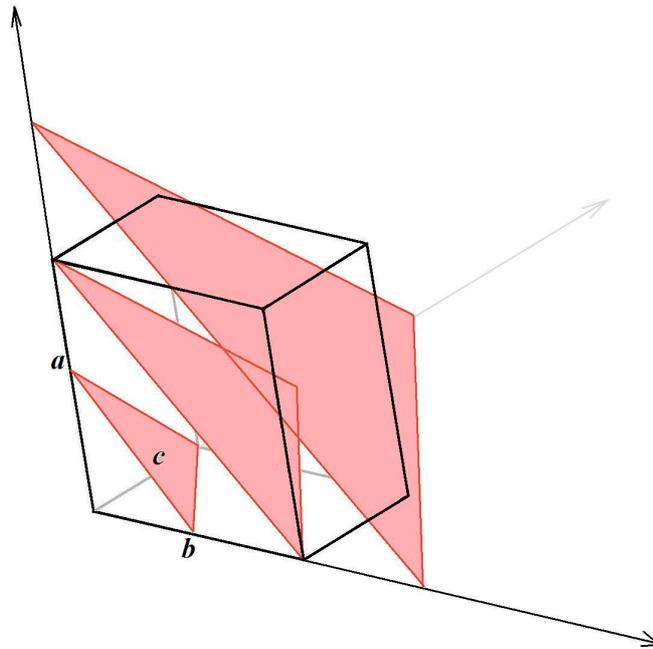
Figure 2.4 A set of parallel planes in a crystal.

In figure 2.4 the set of parallel planes illustrated intersect the *a* axis twice per unit cell, the *b* axis twice and the *c* axis once. Hence this set of planes is termed (221). The value of *n* in the Bragg equation then becomes incorporated into the description of the set of planes i.e. *n* is always taken to be 1.

2.1.4 The Bragg equation reflected in crystal symmetry
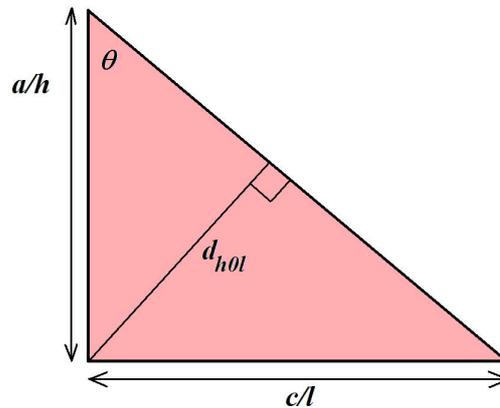
Figure 2.5 A section of a 2-dimensional lattice.

Figure 2.5 shows a section of a 2-dimensional lattice, where *d* is the interplanar spacing, *a* and *c* are the unit cell parameters and *h* and *l* are the Miller indices of the set of planes under consideration. It follows from trigonometry that:

$$\sin\theta = \frac{d_{(h0l)}}{a/h} \tag{2.4}$$

$$\text{and } \cos\theta = \frac{d_{(h0l)}}{c/l} \tag{2.5}$$

Using the relationship $\sin^2\theta + \cos^2\theta = 1$

$$\frac{d_{(h0l)}h^2}{a^2} + \frac{d_{(h0l)}l^2}{c^2} = 1 \tag{2.6}$$

Factorising

$$d_{(h0l)}^2\left(\frac{h^2}{a^2} + \frac{l^2}{c^2}\right) = 1 \tag{2.7}$$

Rearranging

$$\frac{1}{d_{(h0l)}{}^2} = \frac{h^2}{a^2} + \frac{l^2}{c^2} \tag{2.8}$$

By analogy, in three dimensions the equation becomes:

$$\frac{1}{d_{(hkl)}{}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \tag{2.9}$$

This equation represents the orthorhombic system. Combining the above with the Bragg equation $n\lambda = 2d\ sin\theta$ gives:

$$\sin^2\theta_{(hkl)} = Ah^2 + Bk^2 + Cl^2 \tag{2.10}$$

$$\text{where } A = \frac{\lambda^2}{4a^2}, B = \frac{\lambda^2}{4b^2}, C = \frac{\lambda^2}{4c^2}$$

This provides a simple expression relating the angles at which Bragg diffraction can occur and the respective planes giving rise to it. It can be simplified for higher symmetry systems. For the tetragonal system, where $a = b$, the equations become

$$\frac{1}{d_{(hkl)}{}^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \tag{2.11}$$

$$\sin^2\theta_{(hkl)} = A(h^2 + k^2) + Cl^2 \tag{2.12}$$

and for the cubic system, where $a = b = c$, the equations reduce to:

$$\frac{1}{d_{(hkl)}{}^2} = \frac{h^2 + k^2 + l^2}{a^2} \tag{2.13}$$

$$\sin^2\theta_{(hkl)} = A(h^2 + k^2 + l^2) \tag{2.14}$$

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These equations for the orthogonal cells illustrate that Bragg diffraction may occur only at specific angles (or specific interplanar spacings). It is possible to derive selection rules for the Miller indices for different lattices. Table 2.2 shows the possible values of *h*, *k and l* for cubic lattices.

Bravais lattice	Allowed reflections	Forbidden reflections	Examples
Primitive (P)	Any *hkl*	None	CsCl
Body-centred (I)	*h+k+l* even	*h+k+l* odd	Fe
Face-centred (F)	*hkl* all even or odd	*hkl* mixed even or odd	NaCl, Ag

Table 2.2 Values of h, k and l for cubic lattices.

2.1.5 Point groups and space groups

Once the cell type has been identified, the crystal can be assigned to one of the 230 space groups. A space group represents the most specific description possible for a crystal lattice and categorically defines the structure. The symmetry operations present in the lattice are described by the point group (or crystal class), of which there are 32 in total. Any such symmetry operation leaves the structure visually unchanged and at least one point unmoved. They consist of rotation (where the structure is rotated a specific fraction of a circle), reflection (where the structure is reflected through a plane) and inversion (where the signs of co-ordinates are reversed with respect to a centre of symmetry). When the point group operations are combined with certain translational operations, we arrive at the 230 point groups. The relevant translations are a pure translation (moving in a line a certain fraction of a unit cell), a screw axis (rotation followed by translation parallel to the axis of rotation) and a glide plane (translation along a plane then reflection through the plane).

2.2 EXPERIMENTAL DETAILS

2.2.1 The X-ray powder diffraction (XRPD) pattern

The Bragg equation defines the planes, *d*-spacings and directions at which constructive interference occurs with a crystal. For a single crystal of sufficient size, the various reflections can be identified as the detector is moved around the sample. This means that together with a list of angles, interplanar spacings and intensities of the Bragg peaks, the Miller indices of the planes are also known. However, if a single crystal of sufficient size cannot be grown, X-ray powder diffraction (XRPD) is employed. Now rather than a single crystal lattice having one orientation relative to the incident X-ray beam, the bulk sample consists of a large number of randomly oriented microcrystallites. An incident beam may strike a particular set of planes within a microcrystal and Bragg reflection will occur at the corresponding angle. However, the specific direction that the diffracted beam leaves the sample will depend on the orientation of the microcrystal relative to the bulk powder. This is illustrated in figure 2.6.
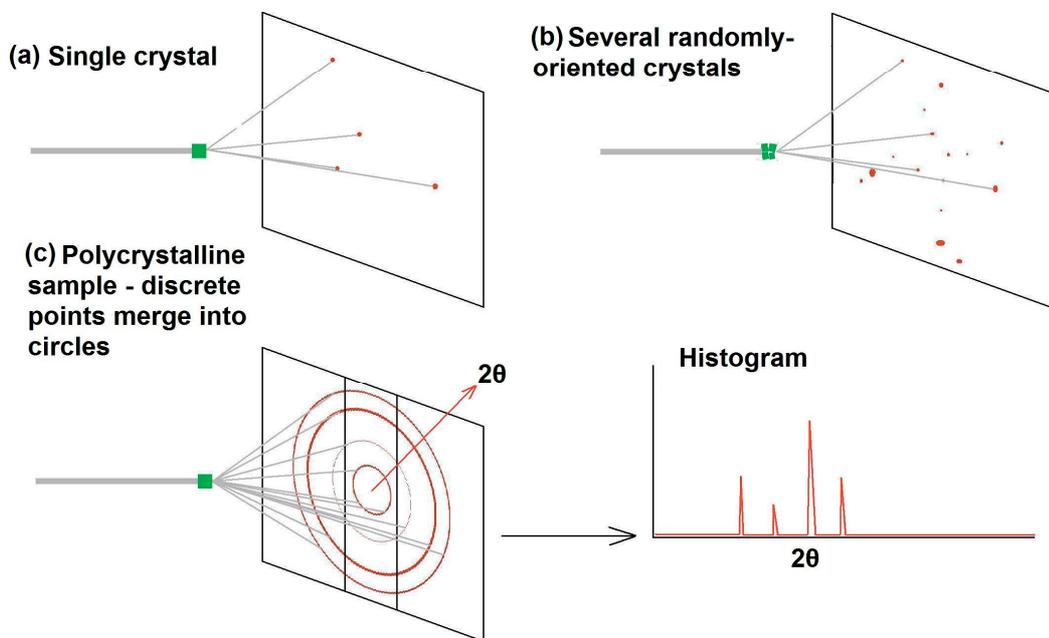
Figure 2.6 X-ray diffraction from a single crystal versus powder.

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Figure 2.6(a) shows an X-ray beam incident on a single crystal. Bragg diffraction occurs from a number of planes and spots are seen on the photographic plate. As in figure 2.1, the Bragg construction, the angle between incident and scattered rays is 2θ. Figure 2.6(b) shows four randomly oriented single crystals. Again Bragg diffraction occurs and four sets of spots now appear on the plate. Figure 2.6(c) shows the effect of placing a polycrystalline material in the beam. The crystallites now lie in every possible orientation, and so each set of parallel planes in the sample gives rise to a cone of scattered radiation with a semi-vertex angle of 2θ. The spots merge into circles where they intersect with the plate, producing so-called Debye-Scherrer rings, named after the camera invented by Debye, Scherrer and Hull. A modern X-ray powder diffractometer measures intensity against 2θ, extending radially from the centre of the circle in figure 2.6(c). With a single crystal there is directional anisotropy as well as angular information to the image. With the powder the directional information is lost and only the angles are measurable. Thus an XRPD pattern consists of a set of 2θ values (readily convertible to d-spacings via the Bragg equation) and the associated intensities of the reflections.

2.2.2 The factors that contribute to a powder pattern

2.2.2.1 Peak position and intensity
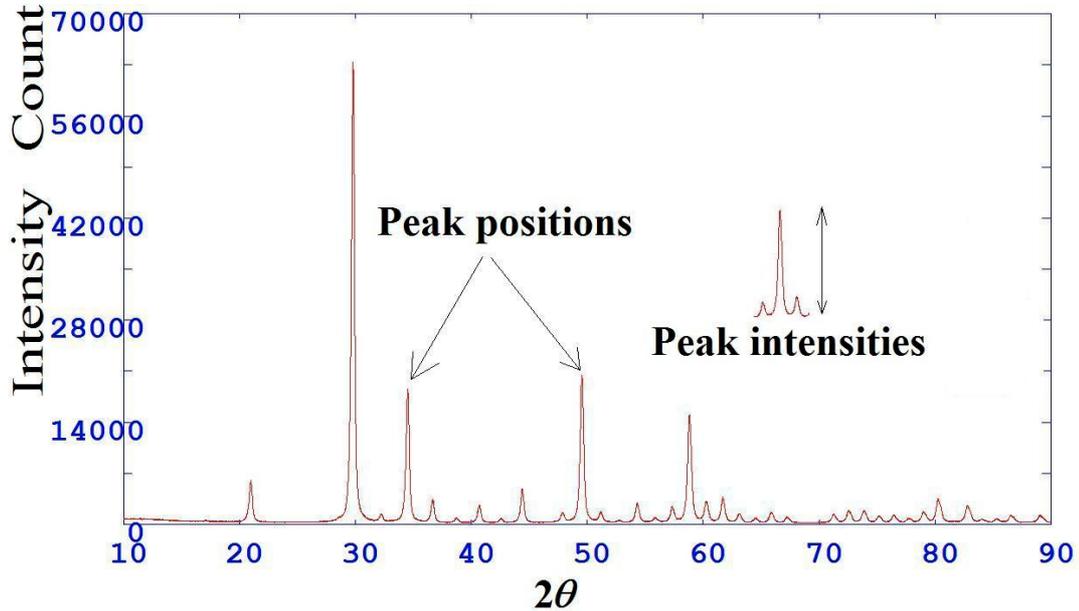
Figure 2.7 Peak positions and peak intensities.

The two most important features of an XRPD pattern are both expressions of the unit cell. These features are illustrated in figure 2.7. Firstly the positions of the peaks in the pattern i.e. the specific angles at which Bragg diffraction can occur are determined solely by the cell type. The unit cell parameters of the lattice generate a series of possible *d*-spacings. Essentially, all XRPD patterns of the same cell type will have the same series of peaks, albeit there will be differences of scale between patterns due to different cell sizes. For example, potassium chloride and elemental silver both have face-centred cubic lattices and so both will have the same series of Miller indices from which Bragg reflections occur. To illustrate how peak positions vary with unit cell parameter, figure 2.8 shows a number of patterns for a cubic cell.
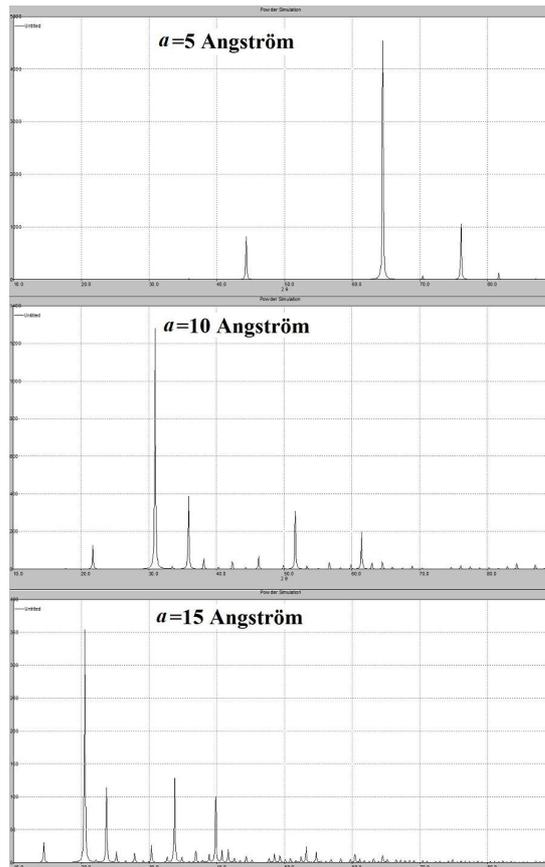
Figure 2.8 How unit cell parameter affects peak positions.

For each cell in figure 2.8 only the unit cell parameter, *a*, has been changed. As the cell shrinks, the magnitudes of the possible interplanar spacings decrease according to the Bragg equation. Hence the angles at which Bragg diffraction occur increase in inverse proportion.

Secondly, the intensities of the peaks are determined by atomic weights and the positions of the atoms in the unit cell. To illustrate how peak intensities are affected by changing the cell contents whilst leaving the peak positions unaffected, figure 2.9 shows 2 XRPD patterns based on the structure of the mineral europia (Eu_2O_3). The top image gives the actual pattern based on the known structure. The second gives a calculated pattern where the europium atoms are replaced by scandium, a much lighter metal with fewer electrons to scatter the incident X-ray beam.
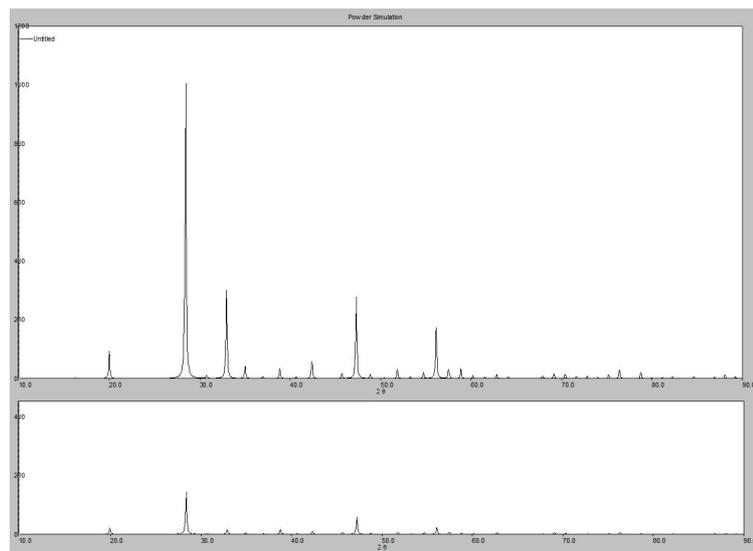
Figure 2.9 How cell contents affect peak intensities. Upper pattern Eu$_2$O$_3$, lower pattern Sc$_2$O$_3$.

Although an ideal powder pattern would contain sharp Bragg reflections, there is always a profile to each peak. The height of the peak is determined by other factors in addition to the atomic positions, the major factors being multiplicity and preferred orientation. Multiplicity is the number of reflections contributing to a peak. If we consider the equation for the cubic cell, $\sin^2\theta_{(hkl)} = A(h^2 + k^2 + l^2)$, it is clear that for some values of 2θ there can be more than one set of planes with the same *d*-spacing. To illustrate this, the (221) planes and the (300) planes both have $h^2 + k^2 + l^2 = 9$. Therefore, some peaks in the pattern are actually the summation of several peaks, but because the diffraction pattern is condensed into the one dimension of 2θ space (compared to the 3 dimensions of a single crystal pattern), these peaks are superimposed and a single peak is recorded. Preferred orientation becomes important when the crystal morphology is elongated in one or more direction. In either case, the material tends to line up in certain directions rather than the random orientation desirable for XRPD. The result is that the intensities of particular peaks will tend to be enhanced. This can be obviated somewhat by grinding the powder sufficiently prior to analysis.

For an ideal powder sample the intensity is given by:

$$I(hkl) = c\ L(2\theta)\ P(2\theta)\ A(2\theta)\ j_{hkl}\ \left| \mathbf{F}(hkl) \right|^2 \qquad\qquad (2.15)$$

where c is a scale factor

L is the geometric (Lorentz) factor

P is the polarisation of the X-ray source

A is the absorption factor

j_{hkl} is the multiplicity of the reflection

$\mathbf{F}(hkl)$ is the structure factor, a measure of the scattering power of the electrons of the unit cell

L, P are correction factors for the diffractometer; A is a correction factor for the sample.

Each atom in the unit cell is surrounded by an electron cloud and it is this that is responsible for the scattering of incident X-rays. The scattering due to all atoms throughout the unit cell is a vector quantity called the structure factor. This vector quantity is a summation over all the atoms in the unit cell and is given by

$$F(hkl) = \sum_n s_n o_n e^{-W_n} e^{(2\pi i(hx_n + ky_n + lz_n))} \qquad\qquad (2.16)$$

where s_n is the atomic scattering length, the ratio of the atom X-ray scattering factor (proportional to atomic number) to the electron radius 2.818×10^{-15} m

o_n is the atomic occupation on a particular site

$\exp(2\pi i\ (hx_n + ky_n + lz_n))$ is the wave interference term

W_n is a thermal factor called the Debye-Waller factor, dependent upon both temperature and atomic displacement.

Whereas the structure factor is a vector quantity and contains phase information, the intensity contains the modulus of the square of the structure factor. Therefore the intensity, which is the quantity measured in a powder pattern, can provide no information on the phases of interfering wavelets. Hence nothing of the cell contents can be inferred directly from the pattern. How the intensity relationship is employed in structure solution will be explained further in 2.3.5.

2.2.2.2 Peak width

Since the electron cloud of an atom has size, scattered X-rays arising from different points on its surface will experience different degrees of interference.
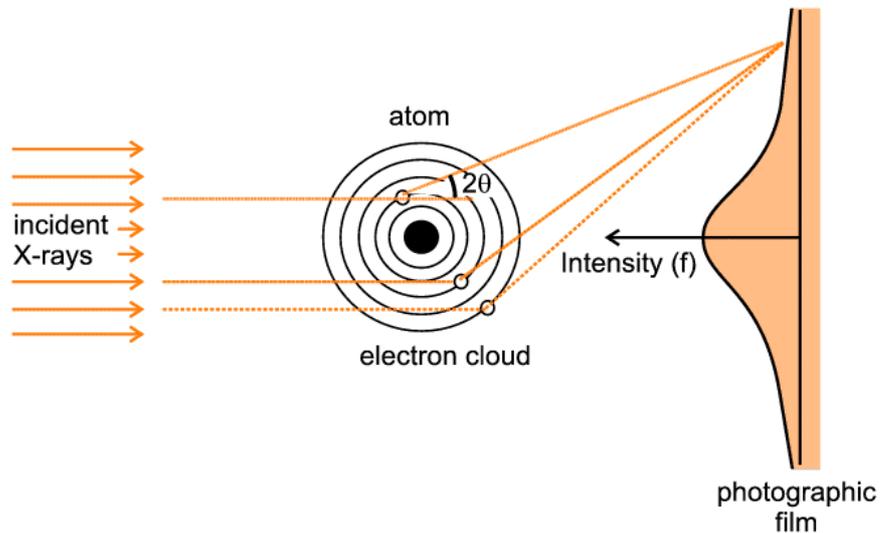
Figure 2.10 Scattering of X-rays by a single atom. Image from
http://pd.chem.ucl.ac.uk/pdnn/peaks/peakcon.htm

Figure 2.10 shows that X-rays leaving the atom from different points may have a different path length to the detector. This is one factor leading to peak widening. Peak width is also determined by the size and strain of the crystallites. Figure 2.11 shows a typical peak.
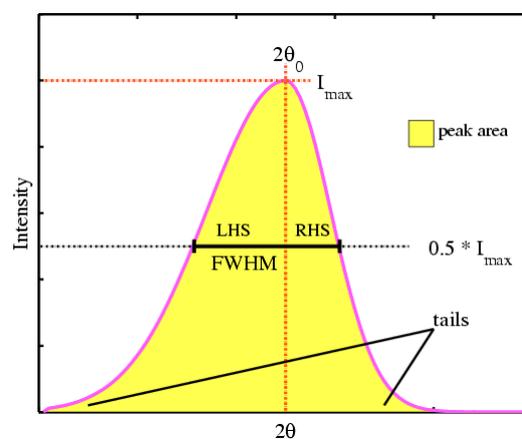
Figure 2.11 A peak from a powder diffraction pattern. Image from
http://pd.chem.ucl.ac.uk/pdnn/peaks/peakcon.htm

Looking at the peak, there are two important features to note. First, the peak has a distribution of intensities rather than a single value. Second, the assigned 2θ value may not occur at the middle of the peak i.e. there may be some asymmetry. The quantity used to measure the peak width is FWHM (full width at half maximum). It is clear from this image that care must be taken to record the pattern as accurately as possible in order that the most appropriate value for 2θ can be determined, as it is the 2θ values that will be used in indexing in order to determine the cell type.

2.2.2.3 Short-range order

The regions between the peaks may contain information about short-range order in the material. This may be important if the material shows only part crystallinity, or is mixed with such a material. This might occur with a polymer, where there is a degree of alignment in a certain direction, but this is not extended through the whole material.

2.2.3 Sources of X-rays

2.2.3.1 The X-ray tube

The modern X-ray tube is in principle no different to the cathode ray tubes employed by Crookes in the late 19th century. Indeed, it was Röntgen's experiments with a Crookes tube in 1895 that led to his discovery of X-rays. An evacuated glass tube has at one end a hot tungsten filament, which, by virtue of its temperature, emits electrons. A large potential difference, of the order of 100kV, is applied across the tube and the electrons are accelerated to the anode, with which they interact. X-rays are then produced, leaving the tube through a window perpendicular to the electron beam. About 1% of the incident energy is converted to X-rays, the rest being converted to heat. Because of the intense heat created in the anode it is mounted on a heat sink, which is cooled with water. A schematic for an X-ray tube is shown in figure 2.12.
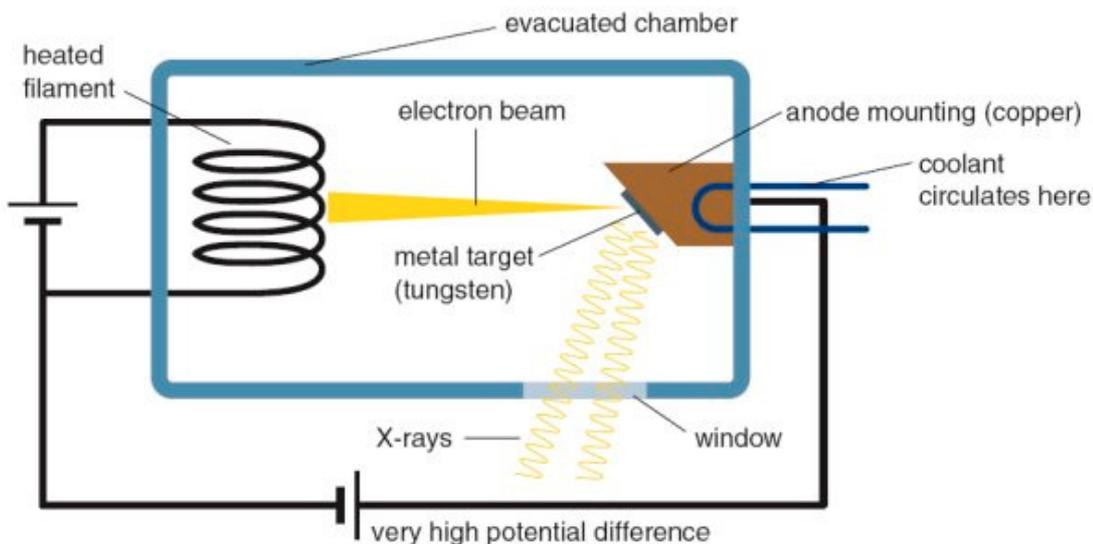
Figure 2.12 The basic elements of an X-ray tube. In this example the anode metal is shown as tungsten.

Image from http://www.genesis.net.au/~ajs/projects/medical_physics/x-rays/

In a vacuum tube, X-rays are generated in two ways. Firstly, the characteristic curve of the emission spectrum, known as white radiation, represents the incident electrons losing kinetic energy in the form of X-rays. This deceleration, caused by the electron interacting with the metal nucleus, can occur over multiple events and so there is a corresponding range of emitted X-ray energies, peaking with the incident electron decelerating in one sudden burst of radiation. The term for this phenomenon is Bremsstrahlung, or 'braking radiation'. Bremsstrahlung refers to any emission of radiation due to change of velocity of a charged particle, for example the generation of synchrotron radiation. However, the term is often used more specifically to identify the white radiation output of an X-ray tube. Figure 2.13 shows a typical X-ray emission spectrum. Secondly, the characteristic spikes in the spectrum are due to specific electron transitions in the atomic orbitals of the anode metal. An incoming electron may knock out a low energy electron, close to the nucleus. A high-energy electron then 'falls back' to replace it, releasing radiation in the form of an X-ray photon. If the drop is to the K shell, the emission is termed Kα or Kβ, depending upon the exact state from which it fell.
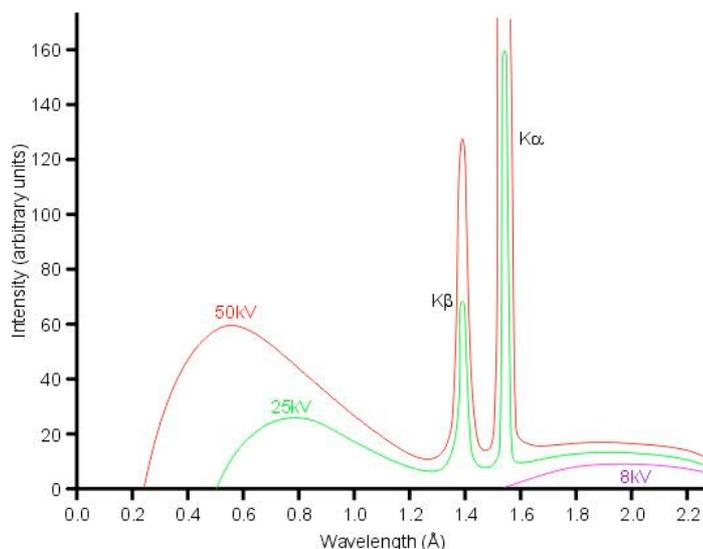
Figure 2.13 An X-ray emission spectrum. Image from
http://pd.chem.ucl.ac.uk/pdnn/inst1/xrays.htm

Characteristic emissions are designated by the name of the shell to which the electron falls back (K, L, M etc). If the transition is between adjacent shells it is termed an α line. If the transition is across 2 shells it is called a β line. It is these specific X-ray energies in the spectrum which are employed in X-ray crystallography and typically the Kα emission is used. A number of transitions are shown in figure 2.14.
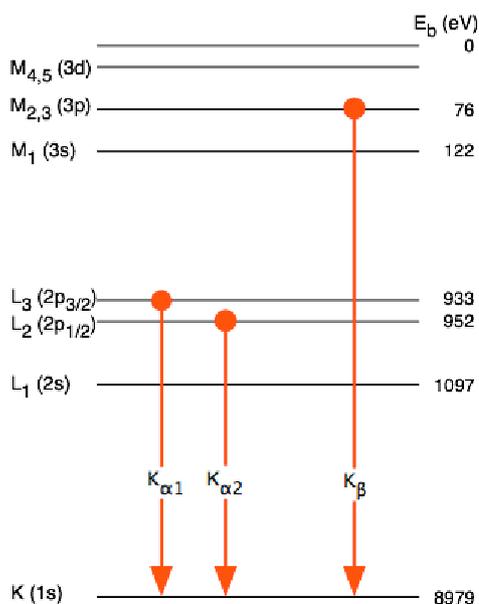
Figure 2.14 Electron transitions giving rise to characteristic X-rays. Image from
http://en.wikipedia.org/wiki/K-alpha

The Kα line results when an electron drops to the K shell (principal quantum number 1) from a 2p orbital of the L shell (principal quantum number 2). The line is actually a doublet, consisting of lines termed Kα_1 and Kα_2. The two lines have slightly different energies, which arise from spin-orbit interaction energy between the electron spin and the orbital momentum of the 2p orbital. The Kα emission is generally the most intense one in the spectrum. For copper, a typical target material, it is about 1.54Å. A list of wavelengths is given in table 2.3.

Element	Kα (weight average)	Kα_2 (strong)	Kα_1 (very strong)	Kβ (weak)
Cr	2.29100	2.29361	2.28970	2.08487
Fe	1.93736	1.93998	1.93604	1.75661
Co	1.79026	1.79285	1.78897	1.62079
Cu	1.54184	1.54439	1.54056	1.39222
Mo	0.71073	0.71359	0.70930	0.63229

Table 2.3 X-ray wavelengths for typical anode metals. All values in Ångströms.

2.2.3.2 Synchrotron source

2.2.3.2.1 Introduction

Synchrotron radiation is emitted when charged particles moving at relativistic speed experience a change in velocity. In practice this is obtained by forcing them to travel in a circuit consisting of straight sections joined by dipole bending magnets. It is the change in direction at each corner of this multi-sided polygon that forces the emission of synchrotron radiation. Modern synchrotron sources are housed in large toroidal buildings and typically have a circumference measured in hundreds of metres.

Synchrotron radiation is emitted in a broad continuum, typically from X-ray to far infra-red. Compared to the X-rays generated in a lab-based powder diffractometer, synchrotron radiation is of high intensity and hence the signal-to-noise ratio is low, giving a high resolution pattern. The synchrotron radiation passes through a double crystal monochromator, from which a specific wavelength can be selected. Thus the output incident beam is highly monochromatic with no Kα couplet and is highly collimated. Peak positions are insensitive to sample shape or incorrect alignment and

peak widths are unaffected by the parafocussing condition as the detector is rotated around the sample. Because of this, peak widths are generally narrow. XRPD patterns obtained via synchrotron radiation are therefore superior in many ways to their lab equivalents.

Photon energies emitted by a synchrotron source are measured in keV rather than Ångströms. This is shown by the equation

$$\lambda \ (\text{Ångström}) \ x \ \text{energy (keV)} = 12.3984 \qquad (2.17)$$

Therefore Cu Kα_1 radiation at 1.54056Å can also be expressed as 8.05 keV.

The synchrotron radiation used in this work was generated at Diamond Light Source, Oxfordshire and collected on beamline I11.
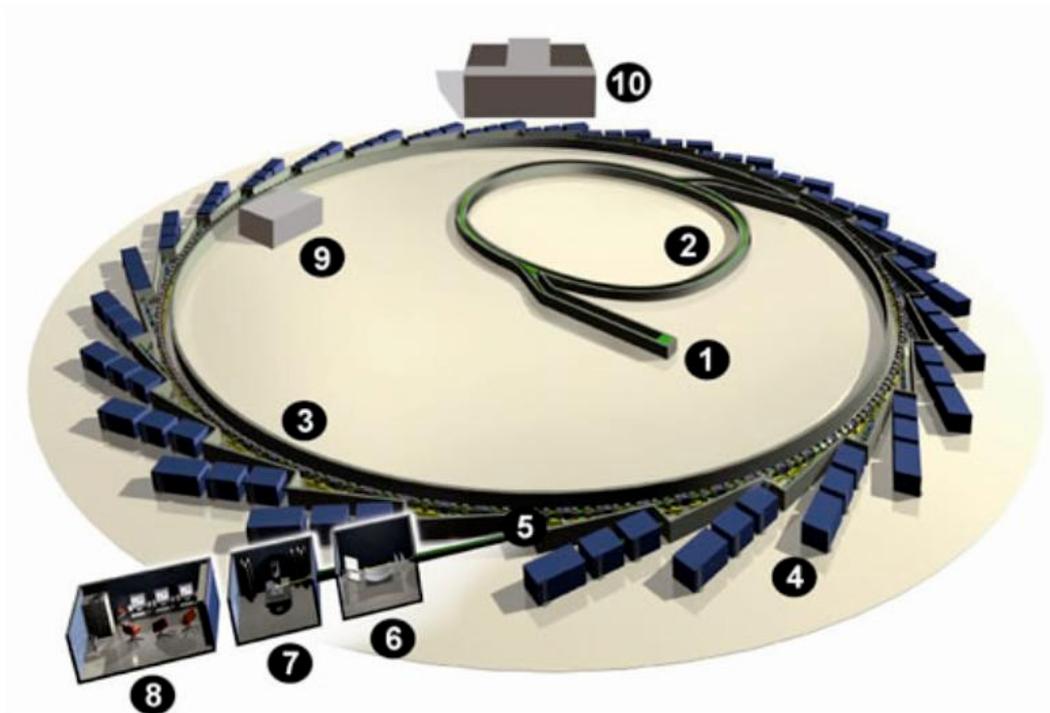
Figure 2.15 Schematic of the Diamond Light Source site. Image from http://www.diamond.ac.uk/Home/Technology/Components/storagering.html

2.2.3.2.2 Parts of the synchrotron machine

There are four main components to the synchrotron source. These are an electron gun to generate low-energy electrons; a linear accelerator (linac) to increase the velocity of the electrons; a small booster synchrotron to accelerate the electrons further before injection into the storage ring; and a storage ring to confine the electrons in orbit and maintain their energy as they generate synchrotron radiation.

The electron gun and linac are essentially the same as the X-ray tube in a powder diffractometer. These are labelled '1' in figure 2.15. Electrons are released by thermionic emission from a hot tungsten cathode under vacuum. From here they are attracted to the anode, but are grouped into bunches by a grid which is turned on and off alternately. As the grid opens, a bunch of electrons passes through before the grid closes again. This bunch is accelerated by the anode to 90keV before entering the 30m linac. Within the linac, the electron bunch is accelerated further by tuning an electric field to its speed. This ensures that the electrons experience a permanently positive field. On exiting the linac, electrons are travelling at near light speed, with an energy of 100MeV before entering the booster synchrotron.

The 158m booster synchrotron, labelled '2', is able to accelerate electrons to an energy of 3GeV before entering the main storage ring. Rather than a regular polygon, it consists of two straight sections and two curved sections, rather like an athletics track. A series of 36 dipole magnets operating at up to 0.8 Tesla are needed to maintain the electron beam around these curves as the energy of the beam increases to its maximum. The electrons are accelerated along the straight sections by a radio-frequency voltage source.

The 561.6m storage ring, labelled '3', actually consists of 24 straight sections connected by a total of 48 bending magnets. Each of these magnets is capable of diverting the electron beam by 7.5°, meaning that a closed orbit is maintained around the building. At an energy of 3GeV, an electron will orbit the ring over 500,000 times per second. The storage ring is under high vacuum to minimise energy loss from the beam striking air molecules and at this pressure the beam lifetime is defined as the time

for the energy to drop to 37% (e^{-1}) of its starting value. This equates to about 20 hours. The beam will eventually dissipate, colliding with the occasional air molecule and eventually with the outer wall of the storage ring. Therefore the beam energy is maintained by use of the linac and booster synchrotron to periodically top up the storage ring. In addition, on each circuit of the ring the electron beam passes through a radio frequency cavity (labelled '9'). This ensures that energy lost as synchrotron radiation via the bending magnets or insertion devices is replaced and the beam orbit is maintained.

Much of the power consumed by the synchrotron machine is due to the bending magnets. Operating at 1.4 Tesla, each coil carries 1,300A of current. The magnetic field and electron energy also determines the continuum of synchrotron radiation. At Diamond, the average energy photons are 8keV.

The electron beam is highly contained; the gap through the bending magnets is only 50mm, whilst the beam itself averages 0.25mm wide and 0.017mm high.

Beamlines at Diamond designated with a 'B' use only the polychromatic synchrotron radiation emitted by the bending magnets at the ends of the straight sections. There are currently 4 'B' beamlines at Diamond. Beamlines designated with an 'I' use insertion devices to stimulate the emission of high-intensity X-rays. These are placed in the straight section before the beamline. They consist of magnets alternately arranged so that the beam experiences a rapid oscillation as it passes the device, analogous to driving a vehicle over a cattle grid at speed. There are two types of insertion device, namely wigglers and undulators, both consisting of magnetic arrays. A wiggler produces a wide spectrum of very high energy X-rays; undulators are more commonly employed and create a narrow energy range of X-rays, which can be changed by adjusting the separation of the magnets.
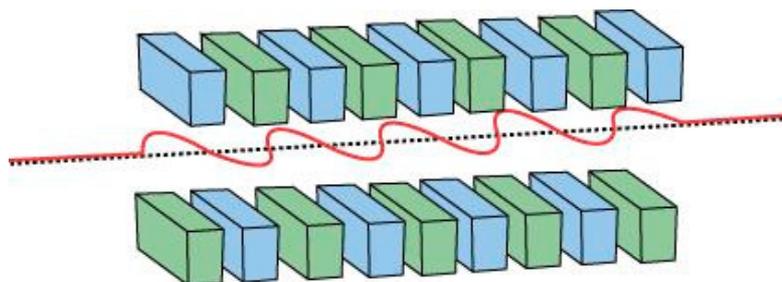
Figure 2.16 Insertion device consisting of alternately-arranged magnets causing the electron beam to oscillate. Image from http://www.diamond.ac.uk/Home/About/FAQs/Science.html#storagering

The various beamlines, labelled '4', are arranged tangentially to the storage ring. These are the points at which synchrotron radiation is emitted, as the electron beam is forced to change direction by the bending magnets. Each beamline consists of 3 sections: an optics hutch ('6') where the particular X-rays required are filtered, an experimental hutch ('7') where the X-rays are incident upon the sample, and a control cabin ('8') where the experimental data is collected.

2.2.3.2.3 Beamline Schematic

The beamline used at Diamond Light Source was I11. A schematic of the beamline is shown below.
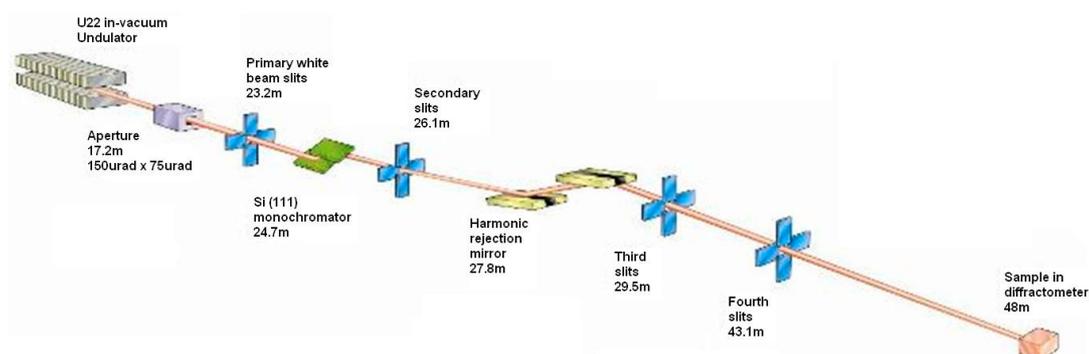
Figure 2.17 Schematic of beamline I11 at Diamond. Image from http://confluence.diamond.ac.uk/display/I11Doc/Technical+Documentation

In its simplest terms an X-ray powder diffractometer is a machine whereby a monochromatic X-ray source is targeted at a microcrystalline sample and the intensity of reflected radiation measured against angle. In principle the source emitting from the tube anode is, of course, polychromatic. It is also divergent and so measures are taken to produce a straight, flat monochromatic beam of a similar width to the sample size. The usual geometry used in a diffractometer is reflection, although some machines employ transmission geometry. The diffractometer geometry used in this work is known as Bragg-Brentano and is shown in figure 2.18. The incident beam and detector move on the circumference of a circle centred on the sample in what is known as a parafocussing mode. The powder sample is held in a shallow, circular well. The powder is pressed into the well and its surface made level with the top of the well. The sample holder is then aligned on the goniometer axis of the diffractometer at an angle θ to the incident beam. The detector, a scintillation counter, rotates around the sample at twice this angle, meaning that a set of readings for 2θ against intensity is obtained. In theory this information is all that is needed to arrive at a full crystal structure for the material, although it will be shown later that this is by no means a straightforward task.
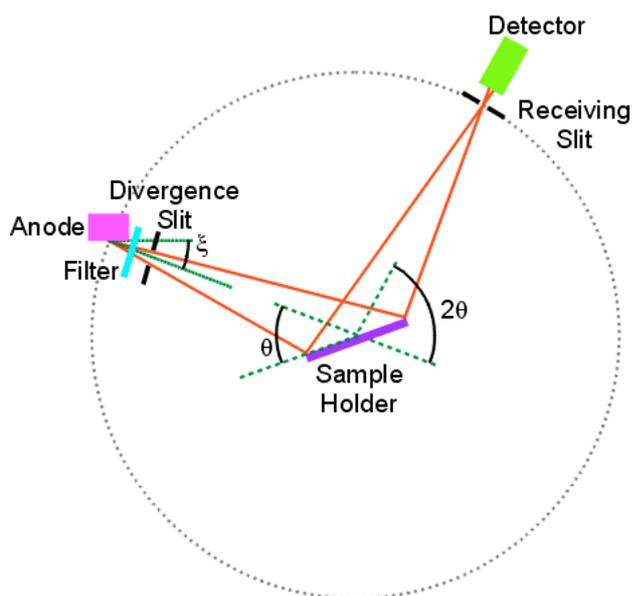
Figure 2.18 Diffractometer with Bragg-Brentano geometry. Image from
http://pd.chem.ucl.ac.uk/pd/welcome.htm

2.2.4.2 The parts of the diffractometer

After leaving the X-ray tube the polychromatic beam strikes the primary monochromator, which consists of a single crystal. The crystal used is oriented such that the Bragg condition is satisfied for radiation at the Kα wavelength. Kαradiation exiting the crystal then passes through a Soller slit. This is a set of metal plates used to slice a single source of X-rays into a series of thinner, parallel beams. The purpose of this is to limit the out-of-plane (axial) divergence of the X-ray beam whilst maintaining a significant width. This means that the beam can be targeted accurately and will strike the full width of the sample. The beam then passes through a divergence slit. As the spread of the beam across the sample increases at low angle, in some diffractometers these slits are variable so that this variation can be compensated for prior to striking the sample. The monochromatic beam then strikes the sample and the diffracted beam passes through an anti-scatter slit and a receiving slit. After passing through another Soller slit the beam strikes the secondary monochromator, if present. The beam then passes through the detector slit to meet the detector, where a scintillant is used to convert X-ray excitation of electrons into visible light. Light photons give rise to an electrical signal, which can be amplified. A schematic of a diffractometer is given in figure 2.19.
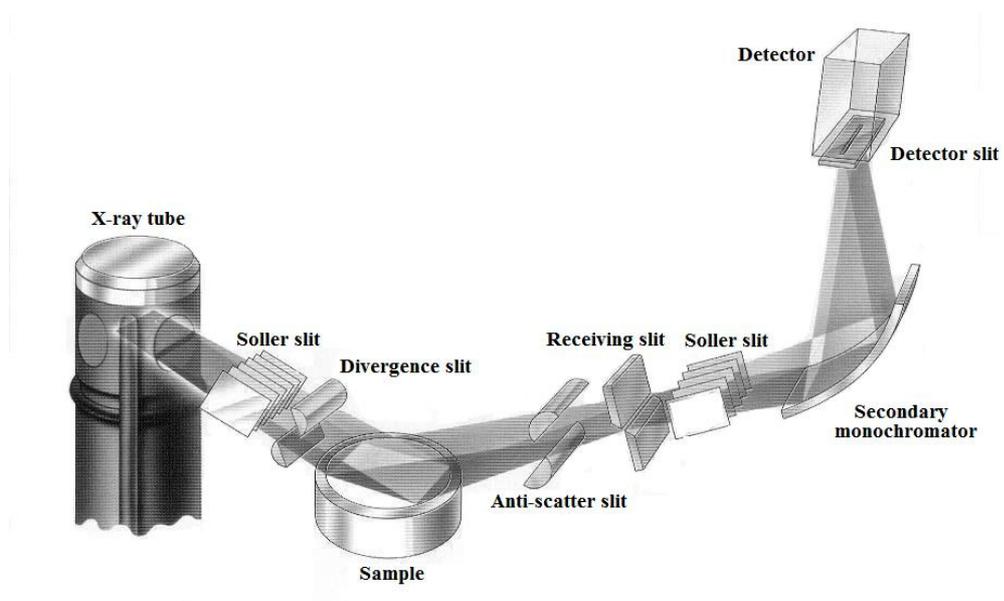
Figure 2.19 Schematic of a powder diffractometer. Image from PANalytical X'Pert manual.

Figure 2.20 shows the PANalytical X'Pert diffractometer used in this work.
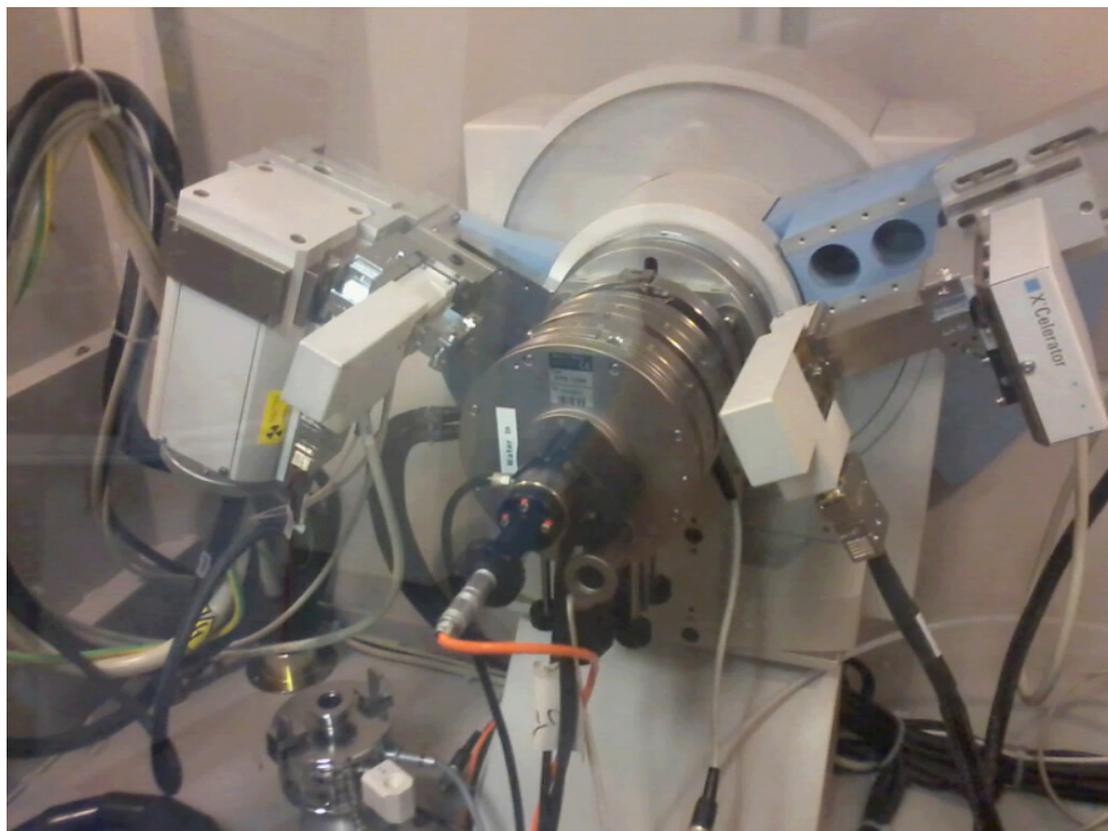
Figure 2.20 PANalytical powder diffractometer.

In the above image the X-ray tube is positioned on the left, identified by the radiation label. The sample holder is inserted from below the central section (steel cylinder) and held in place by four bolts. The incident X-ray beam passes from the X-ray tube into the sample, at an incident angle θ, and exits the sample at an angle 2θ to its original direction. The diffracted beam is then recorded by the detector on the right of the image, marked 'X-Celerator'.

2.2.4.3 Sample preparation

There are a number of issues to consider when preparing a sample for the collection of XRPD data. All are designed to ensure that the reflected beam positions and intensities are representative of the polycrystalline material. Grinding of the powder ensures that particle sizes are similar and small, preferably <10μm. This is essential if peak intensities are to be measured accurately; large differences between crystallite sizes lead to inaccuracies in measured intensities. Grinding can also obviate preferred orientation to a lesser degree.

The sample needs to be flat and level with the sample holder; if not the peaks will be displaced. If the sample is flat but not level with the sample holder then a zero shift can be added to the line peak positions. However, if the sample surface is rough then adding this shift is impracticable. An uneven surface also tends to reduce intensities at low angles.

The sample needs to be of sufficient depth. In this example the well needs to be filled; if not, intensities will again be affected at different angles. In a thick sample the incident beam penetrates the same volume of sample irrespective of angle. At low angle it will only penetrate the sample to a shallow depth but for a longer horizontal distance than if it were at high angle, where it penetrates deeply but not for as long horizontally. This is illustrated in figure 2.21.
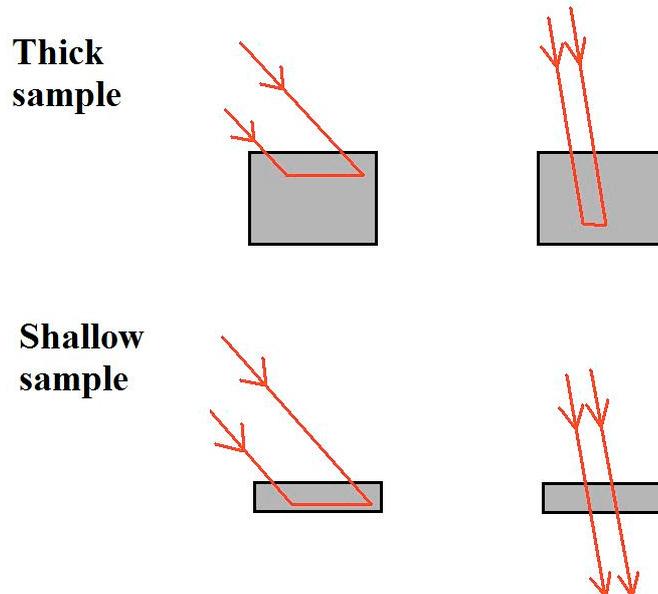
Figure 2.21 Penetration of incident beam into sample.

In figure 2.21, each sample is shown with 2 different incident beams. For the thick sample the volume of material probed by the beam is the same for both angles. For the shallow sample, the high angle beam passes through the sample before the relevant volume is probed. This leads to peak intensity reduction at high angle. Additionally, the incident beam needs to strike within the sample for all angles. If not, the beam overspill at low angle will not give rise to Bragg diffraction and leads to a reduction in peak intensity.

2.2.4.4 Calibration standard

It is common practice to calibrate the diffractometer with a material that has a small number of well-established peaks. In this work the mineral quartz was used. When XRPD data is collected from the standard, any deviation from the expected peak positions will provide the adjustment needed to the peak positions recorded in subsequent diffraction patterns.

2.2.4.5 Data collection

The diffractometer can be set up to scan the sample at a desired rate. In practice there are two factors to consider. Firstly, the 2θ step determines the angle the detector moves between readings. Typically this might be 0.01°. Secondly, for each reading a time to collect the diffracted radiation is stated. This speed would depend on the information required. If the sample was being analysed for the presence of a known structure, a rapid scan could be performed; in this case the signal to noise ratio would not prevent the identification of a set of known peaks in the pattern from the sample. If the sample was of unknown structure then a slow scan would be required, in order to get the sharpest peaks possible which in turn would allow precise determination of their positions and intensities.

2.2.4.6 Output data

The output from the diffractometer consists of values of 2θ and intensity. When plotted these create a histogram, examples of which are given in figures 2.7 to 2.9. It is clear from the images that Bragg diffraction is occurring in certain directions because of the appearance of discrete, sharp peaks in the histogram. From these values for 2θ and intensity, together with the molecular formula, it should now be possible to determine the full crystal structure. This will be explored in the following chapter.

2.3 STRUCTURE DETERMINATION

Crystal structure determination from XRPD data is extremely challenging for a number of reasons. First, as discussed in 2.2.2.1, a powder pattern is essentially a single crystal pattern but compressed into the one dimension of 2θ space. This means that all the directional information obtained from a single crystal diffractometer (i.e. the relevant planes giving rise to Bragg diffraction) is not immediately available, although it is possible to determine this information if the peak positions and intensities can be sufficiently resolved. Whereas a single crystal would generate a single point on the detector for each plane, a polycrystalline sample generates a cone of radiation; where the cone intersects the detector a peak is measured. Second, all planes which have the

same spacing will give rise to superimposed Bragg reflection at the same 2θ position and therefore only one peak is seen. For example, in the cubic system, planes (200), (020) and (002) will give rise to Bragg reflection at the same angle. A knowledge of all possible planes giving rise to the peak is therefore required in order to work back and assign intensities to individual reflections. Third, peaks which are close together may be subject to significant overlap, especially if there are instrumental or sample preparation errors. Peaks may even overlap so much as to be indistinguishable. Fourth, if more than one phase is present then there may be overlap of peaks from unrelated structures. Fifth, once the peak positions are ascertained, the task of assigning Miller indices to the reflections is necessary in order to establish the unit cell. Sixth, in order to index a pattern, an adequate number of peaks needs to be recorded. For many of the automated programs available this number needs to be at least 20. This process of assigning Miller indices to reflections and determining unit cell parameters is called *indexing* and is widely regarded as the most challenging part of the whole process (LeBail and Cranswick 2002). For increasing degrees of freedom this becomes increasingly difficult to perform. For the cubic cell it is usually an easy task, but at the other extreme, the triclinic cell, indexing often fails to find the correct structure; there are so many possible combinations of the 6 unit cell parameters that a multitude of potential cells might be found. This is why it is so important to obtain the best data possible from the diffractometer, particularly establishing with great precision where the peaks lie.

2.3.1 Treatment of data from the diffractometer

2.3.1.1 Raw data

Raw data from the diffractometer consists primarily of a two-column text file containing values for 2θ and intensity. The value of 2θ increase in equal steps, specified at the beginning of the file.

2.3.1.2 Background removal

Based on the known emission profile from the diffractometer, a subtraction from the recorded pattern is made. This has the effect of dropping the peak profiles slightly so that their tails lie on the 2θ axis.

2.3.1.3 Kα_2 stripping

At low angle, the Kα_1 and Kα_2 peaks are closely overlapped. It is possible to mathematically remove the Kα_2 peak, since both their respective wavelengths and the ratio between their intensities are known (see table 2.3). The measured intensity is therefore reduced to take account of this.

2.3.1.4 Peak identification

Bragg peaks are measured as envelopes rather than sharp lines. This necessitates the allocation of an absolute position for the particular line. Generally this is done automatically by peak finding software, although it is possible to assign peak positions manually.

2.3.1.5 Corrections factors

A correction factor $\Delta 2\theta$ can be applied to measured peak positions $2\theta_{obs}$ to determine the theoretical position $2\theta_{calc}$

$$2\theta_{obs} = 2\theta_{calc} + \Delta 2\theta \qquad (2.18)$$

The factors affecting peak position are given by:

$$\Delta 2\theta = \frac{p1}{\tan 2\theta} + \frac{p2}{\sin 2\theta} + \frac{p3}{\tan 2\theta} + p4\sin\theta + p5\cos\theta + p6 \qquad (2.19)$$

where $p1$ and $p2$ are measures of the incident beam axial divergence and peak asymmetry. Axial divergence is corrected by use of Soller slits. Peak asymmetry is caused by the finite detector receiving slit length.

$p3$ is the incident beam in-plane divergence. This arises because the sample is not curved i.e. it does not all fall on the diffractometer focussing circle. However, the effect is small.

$p4$ is the absorption error, which is important for thick samples with low absorption coefficients.

$p5$ is the sample displacement, due to displacement of the sample off the goniometer axis

$p6$ is the zero error, caused by misalignment of the source and detector.

2.3.2 Indexing

Historically there have been two main methods employed for indexing XRPD patterns, namely graphical and arithmetical. Graphical methods work well for high-symmetry systems (cubic, tetragonal, hexagonal). Arithmetical methods may be employed for all symmetry systems, although the chance of success decreases with decreasing symmetry. There has also been some development of software employing global optimisation methods.

2.3.2.1 Graphical methods

The equation relating $\sin^2\theta$ and the Miller indices for the cubic system is:

$$\sin^2\theta_{(hkl)} = A(h^2 + k^2 + l^2) \qquad (2.20)$$

$$\text{where } A = \frac{\lambda^2}{4a^2}$$

The expression shows that for all cubic cells the peak positions will arise in the same distribution, subject to a scaling factor A (which is dependent upon the unit cell parameter, a). That is, the ratios between peak positions for any pattern will be identical. There may be missing peaks due to the particular internal symmetry of the

cell but the essential list of peaks will be the same. Thus, if this peak distribution is found in the diffraction pattern, the presence of a cubic cell can be established. Historically this has been achieved by a graphical method, as shown in figure 2.22.
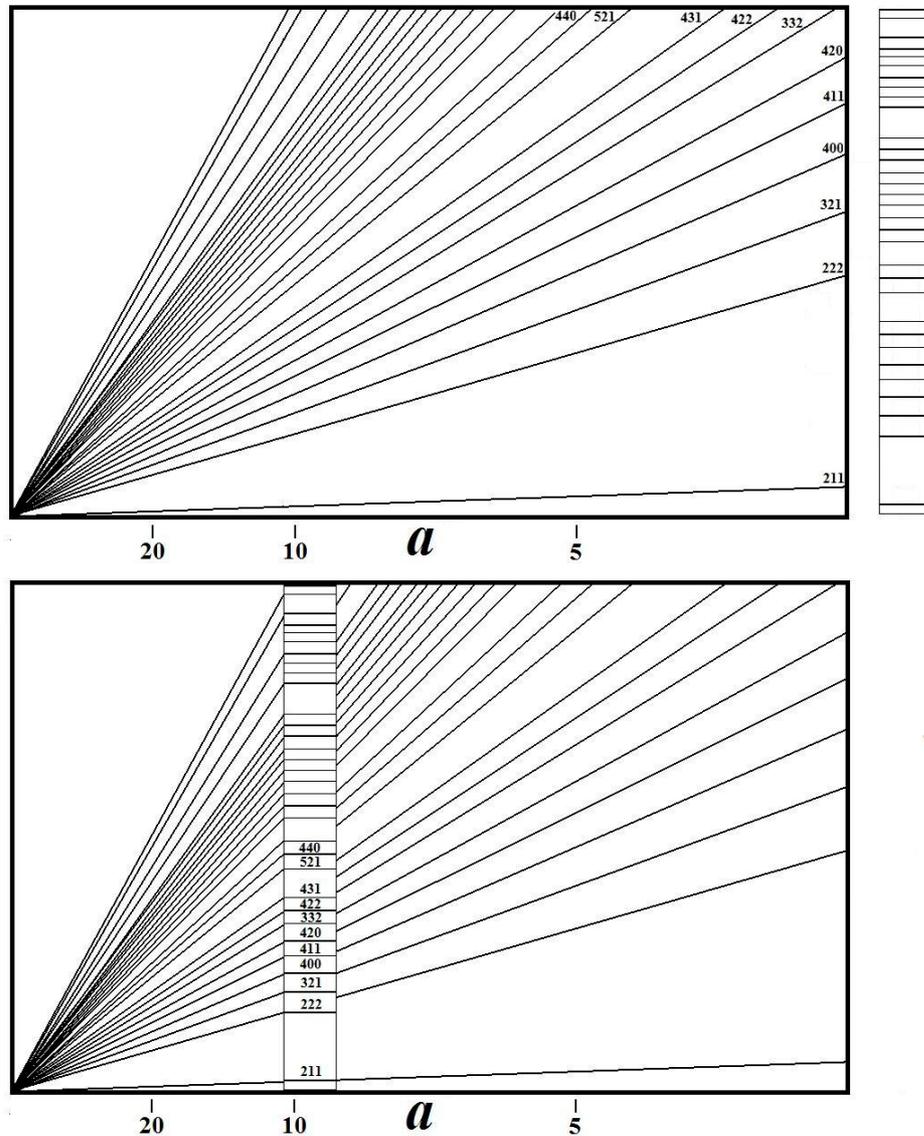
Figure 2.22 A graphical method for indexing the cubic system.

A chart as in figure 2.22 is issued upon which is printed a set of lines corresponding to the possible Miller planes for the cubic system. The spacing of these lines increases as they fan out across the card from left to right, the horizontal axis marked in Ångströms. Each line is marked with its corresponding Miller plane. The relative positions of the recorded Bragg peaks are marked on a thin strip of card which is moved across the chart until the lines on each match up. At this position the corresponding point on the

horizontal axis gives the unit cell parameter. The Miller planes can then be assigned directly from the fan diagram. Similar charts exist for the tetragonal and hexagonal systems. Methods have been developed for determining the tetragonal system (Hull and Davey 1921), (Bjurström 1931), (Bunn 1961). Charts do exist for the orthorhombic system although with increasing degrees of freedom they become increasingly complicated.

2.3.2.2 Arithmetical methods

2.3.2.2.1 Cubic system

Rearranging equation 2.20 gives

$$a = d\sqrt{h^2 + k^2 + l^2}$$

(2.21)

The expression indicates that for the cubic system, there is a relationship between the inter-planar spacing, *d*, of any set of planes (*hkl*) values and the unit cell parameter, *a*. The possible values of $\sqrt{h^2 + k^2 + l^2}$ are known. Therefore if we multiply the highest recorded *d*-spacing by each of these values, a list of possible unit cell parameters is generated. If this is repeated for the next peak, another list of candidate values is obtained. Some of the values in both lists will match. If the process is repeated for subsequent peaks, the list of matching values will eventually collapse to one value, *a*. This is illustrated in table 2.4. The material concerned is iron chromium oxide, JDPDS reference 24-512. The table looks at the first 5 peaks in the XRPD pattern.

hkl	d1	d2	Matches	d3	Matches	d4	matches	d5	Matches
	2.956Å	2.517Å		2.415Å		2.091Å		1.708Å	
100	2.9560	2.5170	8.3608	2.4150	8.3608	2.0910	8.3608	1.7080	8.3608
110	4.1804	3.5596	9.3477	3.4153	11.0603	2.9571	11.8240	2.4155	
111	5.1199	4.3596	10.6580	4.1829	11.8240	3.6217	12.5413	2.9583	
200	5.9120	5.0340	11.0603	4.8300	12.5413	4.1820		3.4160	
210	6.6098	5.6282	11.8240	5.4001	14.4814	4.6756		3.8192	
211	7.2407	6.1654	12.5413	5.9155	14.7800	5.1219		4.1837	
220	8.3608	7.1192	13.5461	6.8307		5.9142		4.8310	
300	8.8680	7.5510	14.4814	7.2450		6.2730		5.1240	
310	9.3477	7.9595	15.0727	7.6369		6.6123		5.4012	
311	9.8039	8.3479		8.0096		6.9351		5.6648	
222	10.2399	8.7191		8.3658		7.2434		5.9167	
320	10.6580	9.0752		8.7074		7.5392		6.1583	
321	11.0603	9.4178		9.0361		7.8238		6.3908	
400	11.8240	10.0680		9.6600		8.3640		6.8320	
322	12.1879	10.3779		9.9573		8.6214		7.0423	
330	12.5413	10.6787		10.2460		8.8714		7.2464	
331	12.8849	10.9714		10.5267		9.1145		7.4450	
420	13.2196	11.2564		10.8002		9.3512		7.6384	
421	13.5461	11.5343		11.0669		9.5822		7.8270	
332	13.8649	11.8058		11.3274		9.8077		8.0112	
422	14.4814	12.3307		11.8310		10.2438		8.3675	
430	14.7800	12.5850		12.0750		10.4550		8.5400	
431	15.0727	12.8342		12.3141		10.6621		8.7091	
333	15.3598	13.0787		12.5487		10.8652		8.8750	
432	15.9185	13.5545		13.0052		11.2604		9.1979	
440	16.7217	14.2383		13.6613		11.8285		9.6619	
441	16.9809	14.4591		13.8731		12.0119		9.8117	
433	17.2363	14.6765		14.0817		12.1925		9.9593	
442	17.7360	15.1020		14.4900		12.5460		10.2480	
443	18.9276	16.1167		15.4635		13.3889		10.9365	

Table 2.4 Arithmetical derivation of unit cell parameter for a cubic cell. All values are in Ångströms.

Although it is possible to work in terms of *d*-spacings and Miller indices for cells of high symmetry, using the relationship between $\sin^2\theta$ and the Miller indices is a useful method for dealing with all crystal systems. Recalling equation 2.20, the relation between $\sin^2\theta$ and the Miller indices:

$$\sin^2\theta_{(hkl)} = A(h^2 + k^2 + l^2)$$

$$\text{where } A = \frac{\lambda^2}{4a^2}$$

This equation shows a relationship between the sum of the squares of the possible Miller indices in the cubic system and the angle at which diffraction occurs. For each peak the value of $\sin^2\theta$ can be determined. If the cell is cubic there should be found whole number ratios between the values of $\sin^2\theta$. For example, if the (400) and (200) reflections are present, then the ratios of their corresponding $\sin^2\theta$ values should be 4:1. This method of indexing is suggested by D'Eye and Wait (D'Eye and Wait 1960) and an example of this process is shown in table 2.5.

Line	2θ	$\sin^2\theta$	ratio to 0.006444	INTEGER ratio	hkl	$\sin^2\theta$ calc	ABS difference
1	15.9800	0.0193	3.0000	3	111	0.0193	0.0000
2	18.4700	0.0258	3.9963	4	200	0.0258	0.0000
3	26.2600	0.0516	8.0120	8	220	0.0516	0.0001
4	30.8000	0.0706	10.9483	11	311	0.0709	0.0003
5	32.2500	0.0772	11.9741	12	222	0.0773	0.0002
6	37.3700	0.1027	15.9321	16	400	0.1031	0.0004
7	42.0000	0.1285	19.9374	20	420	0.1289	0.0004
8	46.2500	0.1543	23.9434	24	422	0.1547	0.0004
9	49.2600	0.1737	26.9611	27	333	0.1740	0.0003
10	54.1300	0.2071	32.1353	32	440	0.2062	0.0009
	SUM	1.0107		157			
	Estimated A	0.0064					
	Refined A	0.0064					
	a	9.6005					

Table 2.5 Arithmetical method for indexing the cubic system.

Looking at the list of $\sin^2\theta$ values, if the ratio of each peak to peak 1 is taken, the first and second ratios are 1 and 1.33 respectively, meaning that the divisor is smaller than the value of $\sin^2\theta$ for line 1. By scaling up from 1 and 1.33 we can take the ratios to be 3 and 4, making the divisor one third of the first $\sin^2\theta$ i.e. the divisor (the constant A) is taken to be 0.06444. Dividing throughout gives ratios close to whole numbers. The value of A can be refined by calculating:

$$A = \frac{\sum \sin^2 \theta}{\sum ratio} \tag{2.22}$$

The unit cell parameter is then calculated from the relationship $A = \frac{\lambda^2}{4a^2}$. The lower is the difference between experimental and calculated values for $\sin^2 \theta$ then the more likely it is that the pattern has been indexed correctly. D'Eye and Wait recommend that differences up to 0.0005 can be accepted but state that poor correlation is often due to the weaker intensities in the pattern which have a lower accuracy of measurement than the stronger lines. It is therefore essential that an XRPD pattern is measured accurately. In this case, all differences except for that of line 10 are less than 0.0005, which implies that the system is indeed cubic.

2.3.2.2.2 Tetragonal system

For the tetragonal system the relationship becomes:

$$\sin^2 \theta_{(hkl)} = A(h^2 + k^2) + Cl^2 \tag{2.23}$$

the volume of the unit cell being a^2c

A method used for the indexing of tetragonal and orthorhombic systems (D'Eye and Wait 1960) is based on two sources (Hesse 1948), (Lipson 1949). Hesse states that the indexing of tetragonal photographs has been successful in several cases where he did not know the crystal system. His method is to look for ratios in the lines where one of the Miller indices is zero, for example the $hk0$ planes. The relationship would then be simplified to $\sin^2 \theta_{(hk0)} = A(h^2 + k^2)$. The first possible nine values of $\sin^2 \theta_{(hk0)}$ for these planes are shown in table 2.6.

hk0	100	110	200	210	220	300	310	320	330
$\sin^2\theta$	A	$2A$	$4A$	$5A$	$8A$	$9A$	$10A$	$13A$	$18A$

Table 2.6 Arithmetic method for indexing the tetragonal system.

It can be seen that ratios of two occur between the first and second values, the second and third values, and the third and fifth values, and so on. In fact, there are a total of five ratios of two for these nine lines. This ratio of two cannot occur in any other system other than the cubic and the tetragonal. Assuming the cubic system has been discounted, it is likely that the system is tetragonal and an attempt can be made at finding the other constant, C. In the above case, because the plane (100) was present, the constant A was identifiable as the smallest factor to give a ratio of two. However, if this line had been absent and the first line had been due to the (110) plane, the lowest factor would have been $2A$. If the first line was due to the (200) plane then the lowest factor would have been $4A$. It is important to be aware that a value that appears to be A may in fact be a multiple of A, otherwise known as a *harmonic*; if the pattern cannot be indexed satisfactorily, the value may be divided by two and then re-tested. If necessary it may be divided by four, and so on.

The method for finding C is to subtract all possible values for $A(h^2 + k^2)$ from the observed lines. For example, subtracting $2A$ from the $\sin^2\theta_{(hkl)}$ for a (201) line would give C, or subtracting $5A$ from the $\sin^2\theta_{(hkl)}$ for a (212) line would give $4C$. Values of A, $2A$, $4A$, $5A$, $8A$ etc are subtracted from the values of $\sin^2\theta_{(hkl)}$ to leave a value of C (or $4C$, $9C$, $16C$ etc depending on the Miller indices for the plane giving rise to line 1) somewhere in each column of the difference table. In addition, there will be multiples of A present due to subtractions from $hk0$ lines.

For each possible value of A there may be several possible values of C. Using each pair of A and C, theoretical $\sin^2\theta_{(hkl)}$ values are calculated by using all possible Miller indices for the tetragonal system and are then compared against the experimental values. The combination of A and C that gives the highest number of matches is likely to be the correct combination. The values of the constants and hence the unit cell parameters can then be refined.

2.3.2.2.3 Hexagonal system

For the hexagonal system the equation is:

$$\sin^2\theta_{(hkl)} = A(h^2 + hk + k^2) + Cl^2 \qquad (2.24)$$

where $A = \dfrac{\lambda^2}{3a^2}$ and $C = \dfrac{\lambda^2}{4c^2}$, the volume of the unit cell being $a^2c \sin\theta$

2.3.2.2.4 Orthorhombic system

For the orthorhombic system the relationship is:

$$\sin^2\theta_{(hkl)} = Ah^2 + Bk^2 + Cl^2 \qquad (2.25)$$

The volume of the unit cell is given by *abc*.

The orthorhombic system is an example of an intermediate symmetry order and tends to be the cut-off point between the likelihood of success or failure with manual indexing methods. It has been shown that the cubic and tetragonal systems can be recognised by a constantly recurring factor, or by ratios of 2 appearing in the $\sin^2\theta_{(hkl)}$ values. For the orthorhombic system there are no such relationships but, as Hess states, this may be overcome if enough lines are present. The general equation for the orthorhombic system has 3 constants. If all three constants are unknown it is necessary to break the equation down using the lines of the pattern. The *A* component is only dependent on *h*, the *B* component on *k* and the *C* component on *l*. This generates the following relationships:

$$\sin^2\theta_{(h00)} = Ah^2 \qquad (2.26)$$
$$\sin^2\theta_{(0k0)} = Bk^2 \qquad (2.27)$$
$$\sin^2\theta_{(00l)} = Cl^2 \qquad (2.28)$$

Therefore:

$$\sin^2\theta_{(hk0)} = Ah^2 + Bk^2 \tag{2.29}$$

Because each Miller index has its own constant, the values of Ah^2, Bk^2 and Cl^2 can be treated independently. Additions of $\sin^2\theta_{(hkl)}$ values of lines, each with two indices of zero, can be done to generate the $\sin^2\theta_{(hkl)}$ value of some other line. For example $\sin^2\theta_{(100)} = A$, $\sin^2\theta_{(010)} = B$ and $\sin^2\theta_{(001)} = C$

This leads to equations of the following types:

$$\sin^2\theta_{(110)} = \sin^2\theta_{(100)} + \sin^2\theta_{(010)} = A + B \tag{2.31}$$

$$\sin^2\theta_{(011)} = \sin^2\theta_{(010)} + \sin^2\theta_{(001)} = B + C \tag{2.32}$$

$$\sin^2\theta_{(101)} = \sin^2\theta_{(100)} + \sin^2\theta_{(001)} = A + C \tag{2.33}$$

$$\sin^2\theta_{(111)} = \sin^2\theta_{(100)} + \sin^2\theta_{(010)} + \sin^2\theta_{(001)} = A + B + C \tag{2.34}$$

and generally:

$$\sin^2\theta_{(hkl)} = \sin^2\theta_{(h00)} + \sin^2\theta_{(0k0)} + \sin^2\theta_{(00l)} = Ah^2 + Bk^2 + Cl^2 \tag{2.35}$$

Therefore, if two or three lines at the low angle end of the pattern can be added together to produce a third line it is likely that the first two lines corresponded to planes having two Miller indices equal to zero. However, the chance of there being all (100), (010) and (001) planes in the pattern is low. It would be useful to make use of the subtraction of lines, thereby generating a much better chance of finding at least one of the constants. Rewriting the above equations:

$$\sin^2\theta_{(100)} = \sin^2\theta_{(110)} - \sin^2\theta_{(010)} = A \tag{2.36}$$

$$\sin^2\theta_{(100)} = \sin^2\theta_{(101)} - \sin^2\theta_{(001)} = A \tag{2.37}$$

and generally:

$$\sin^2\theta_{(100)} = \sin^2\theta_{(1kl)} - \sin^2\theta_{(0kl)} = A \tag{2.38}$$

Equations of a similar type can be written for B and C. If a difference table is set up

such that each $\sin^2\theta_{(hkl)}$ value is subtracted from every other value there should arise recurring differences. The differences that occur most frequently are likely to be one or more of the constants.

However, if insufficient lines are present, the recurring numbers may all be harmonics. These multiples will not necessarily be of magnitude 4, 9, 16, 25 etc as the multiplier is generated by subtraction of two lines. The possible multipliers produced by the subtraction of two square numbers are 3, 4, 5, 7, 8, 9, 11, 12, 15, 16, 20, 21, 24, 25, 32, 35, 36 etc. If a number recurs but does not generate another constant when used as below, then it may be one of these multiples. Dividing by each multiple in turn and testing for generation of another constant should locate the first constant.

Once the first constant has been found, a second can be found, again by a process of subtractions. For ($hk0$) lines the quadratic form can be written as $\sin^2\theta_{(hkl)} - Bk^2 = Ah^2$. Subtracting values of Bk^2 from $\sin^2\theta$ should generate A or a multiple of A

It should now be relatively easy to find C. To do this, values of $Ah^2 + Bk^2$ are subtracted from $\sin^2\theta$. Any recurring values in the table should be equal to C, $4C$, $9C$ etc. Once a choice of constants has been decided upon, an attempt can be made at indexing the diffraction pattern.

Compared with the relatively straightforward use of graphical charts, the manual arithmetical indexing of XRPD patterns is not always a straightforward problem and often relies on some degree of intuition on the part of the investigator. To write a computer program to automatically index a pattern, even one of orthorhombic symmetry, is a substantial task. The methods employed so far approach the problem from the high symmetry end. If the pattern cannot be indexed on a cubic cwll then the system of next lowest symmetry is looked for. For each system the task becomes increasingly difficult, until the problem is either solved or abandoned. The following sections discuss methods that approach the problem from the low symmetry side.

2.3.2.2.5 Monoclinic system

For the monoclinic system the equation is:

$$\sin^2\theta_{(hkl)} = Ah^2 + Bk^2 + Cl^2 - Dhl \tag{2.39}$$

where $A = \dfrac{\lambda^2}{4a^2\sin^2\theta}, B = \dfrac{\lambda^2}{4b^2}, C = \dfrac{\lambda}{4c^2\sin^2\theta}$ and $D = \dfrac{\lambda^2\cos\theta}{2ac\sin^2\theta}$, the volume of the unit cell being $abc(1 - \cos^2\theta)$

2.3.2.2.6 Triclinic system

For the triclinic system the equation for $\sin^2\theta$ is written in terms of the reciprocal lattice:

$$\sin^2\theta_{(hkl)} = \lambda^2/4(h^2a^{*2} + k^2b^{*2} + l^2c^{*2} + 2klb^*c^*\cos\theta^* + 2hlc^*a^*\cos\theta^* + 2hka^*b^*\cos\theta^*) \tag{2.40}$$

where $a^* = \dfrac{bc\sin\alpha}{V}, \cos\alpha^* = \dfrac{\cos\beta\cos\gamma - \cos\alpha}{\sin\beta\sin\gamma}$

$b^* = \dfrac{ac\sin\beta}{V}, \cos\beta^* = \dfrac{\cos\alpha\cos\gamma - \cos\beta}{\sin\alpha\sin\gamma}$

$c^* = \dfrac{ab\sin\lambda}{V}, \cos\gamma^* = \dfrac{\cos\alpha\cos\beta - \cos\gamma}{\sin\alpha\sin\beta}$

the volume of the unit cell given by:

$$V = abc\,(1 + 2\cos\alpha\,\cos\beta\,\cos\gamma - \cos^2\alpha - \cos^2\beta - \cos^2\gamma)$$

The expression for the triclinic system is the equation from which most of the auto-indexing methods in current use are derived. Its use makes no assumptions about the

symmetry of a material under investigation. The complexity of the equation illustrates that recognition of the cell type for the triclinic system from XRPD data alone is a problem of formidable complexity. A number of methods attempt this task (Ito 1949), (DeWolff 1957), (Visser 1969). Arithmetical methods work well for crystal systems up to orthorhombic and can be extended to the monoclinic system, although successful indexing is not always certain. For systems of the lowest symmetry these approaches often fail to provide a general solution to the problem.

The method for the cubic system in 2.3.2.2.1 was that used by the program GRAPHPRO in chapter 7. Another program has been written by the author and has proved successful for orthogonal systems.

2.3.2.3 The indexing suite

In 1999 an attempt was made to bring together a number of indexing programs into one user-friendly format. This has developed into the CRYSFIRE indexing suite (Shirley 2002). CRYSFIRE works by allowing the user to input observed Bragg reflections via a graphical user interface. Reflections may be entered as either 2θ values or as *d*-spacings. Nine indexing programs, including the widely-used ITO (Visser 1969), TREOR (Werner *et al* 1985) and DICVOL (Louër and Boultif 2004) can be individually selected and applied to the data. Each possible solution consists of a set of unit cell parameters and is awarded a figure of merit. CRYSFIRE puts all candidate solutions into a single file so that results from each indexing program can be compared and then loaded into other software such as CHECKCELL to look for the best fit to the experimental data. CRYSFIRE, its indexing programs and CHECKCELL will be discussed further in chapter 5.

Indexing programs make use of the relationship:

$$\frac{1}{d_{hkl}^2} = (r_{hkl}^*)^2 \tag{2.41}$$

where r^* is the reciprocal lattice vector.

The quantity $\dfrac{1}{d_{hkl}^2}$ is referred to in crystallography as Q_{hkl}. The expressions for Q_{hkl} according to crystal system are given in table 2.7.

Cell type	Q_{hkl}
Cubic	$(h^2 + k^2 + l^2).a_{11}$
Tetragonal	$(h^2 + k^2).a_{11} + l^2.a_{33}$
Hexagonal	$(h^2 + hk + k^2).a_{11} + l^2.a_{33}$
Orthorhombic	$h^2.a_{11} + k^2.a_{22} + l^2.a_{33}$
Monoclinic	$h^2.a_{11} + k^2.a_{22} + l^2.a_{33} + hl.a_{13}$
Triclinic	$h^2.a_{11} + k^2.a_{22} + l^2.a_{33} + kh.a_{12} + kl.a_{23} + hl.a_{13}$

Table 2.7 Values of Q_{hkl} expressed using reciprocal unit cell parameters

where $a_{11} = a^{*2}$, $a_{22} = b^{*2}$, $a_{33} = c^{*2}$, $a_{12} = a^* b^* \cos \gamma^*$, $a_{13} = 2a^* c^* \cos \beta^*$ and $a_{23} = 2b^* c^* \cos \alpha^*$

The expressions in table 2.7 are visually similar to those for $\sin^2 \theta$ and are the ones used in most indexing programs.

2.3.3 Assigning the space group

Once the unit cell has been established, the next task is to assign it to one of the 230 space groups. The cell type and the systematic absences in the Miller indices should provide sufficient information for a list of trial space groups to be arrived at. For the purpose of this work, the program Checkcell was used to find the most likely space group.

2.3.4 Establishing the atom positions

The cell and space group is sufficient information to generate a list of peak positions. However, it is the set of atomic positions which determines the intensities of the peaks. There are a number of ways by which this information can be obtained, but the main method used in this work was to look at a similar structure. If a material under

investigation is part of a series, or similar structures are known, these structures can be used as starting points for the unknown structure. For example, many of the rare earth oxides exhibit a monoclinic phase at high temperature. If the structure for gadolinia is not known we could turn to its immediate neighbours europia and terbia and use their known structures as starting points. If the unit cell parameters follow the lanthanide contraction, we could reasonably expect the atoms in gadolinia to lie at the same points.

With the advent of computers with fast processing speeds, it has become possible to work out structures *ab initio*, that is, without any prior knowledge of possible atom positions. Global optimisation is a way of reaching a good approximation to a solution when exploring a large search space. All global optimisation methods begin with a series of trial structures. These are generated by randomly populating the unit cell with atoms, so long as the known empirical formula and density are complied with. For each structure a theoretical diffraction pattern is created and compared with the measured pattern. A measure of fitness is then applied to each trial structure. It is these measures of fitness which determine whether a trial structure is rejected, or accepted and used as the basis for the next generation of trial structures. After many iterations the objective is to converge upon a single solution. In principle this can be difficult for a number of reasons, most notably the problem of becoming trapped in local minima. For this reason, there is provision in the software for random new structures to be introduced even when convergent solutions are evident.

Monte Carlo methods are essentially trial and error algorithms using random numbers. The most widely used Monte Carlo algorithm is the Metropolis-Harrison algorithm. Originally proposed in 1953 (Metropolis 1953) it was first employed in crystal structure determination in the 1990s (Harris *et al* 1994). A Monte Carlo method is used in the programs ESPOIR (Le Bail 2001) and Fullprof (Rodriguez-Carvajal 1993). It is also the basis for the indexing program McMaille (Le Bail 2006).

Simulated annealing is a specific Monte Carlo method. It models a process employed in the heat treatment of metals, where a material is heated and then cooled slowly. This has the effect of allowing unfavourable jumps at high energy, but as the temperature falls, these jumps become less likely. Although a jump in the 'wrong' direction is

unfavourable if it results in a lower fit for the new structure, it is encouraged more at higher temperature. The longer the time the algorithm is run for and the slower the rate of cooling, the better the result should be. Simulated annealing has been applied to structure solution (Kirkpatrick *et al* 1983), (Černý 1985) and is employed by structure solution programs such as DASH (David *et al* 2006) and Fox (Favre-Nicolin and Černý 2002).

The genetic algorithm is a subset of the methods termed *evolutionary algorithms*. Rather than modelling their operation on thermodynamic processes as with the Monte Carlo method, they employ phenomena seen in nature such as inheritance and mutation. The system being studied is encoded in strings called chromosomes, usually as binary 1s and 0s. As with the Monte Carlo method, a means of generating starting structures is employed and these are all given some measure of fitness to the solution. A percentage of these structures, again including some with poor fit, are then selected for reproduction. Two or more parent strings are combined to generate an offspring string. This could be by randomly varying a part of the string (mutation) or crossover (cutting the chromosomes at a specific point and splicing them together). This new generation is then tested for fitness to the solution and the algorithm continues, again always including some poor fits to avoid local minima. Genetic algorithms were first used in crystal structure determination in the 1990s (Harris *et al* 1998).

2.3.5 Full profile refinement

2.3.5.1 Introduction

Once the atomic positions have been established with some accuracy the final stage in the process of structure solution is full profile refinement. Rietveld's method (Rietveld 1969) was the method used in this work. The approximate crystal structure (unit cell and atom positions) combined with information on the instrument (such as zero shift, axial divergence and a background factor) together with adjustments for structural parameters (such as thermal motion and preferred orientation) are used to generate a theoretical diffraction pattern. A method of fit is used to compare this to the experimental pattern and the various parameters then varied using least squares

refinement in order to bring this calculated pattern as close to the experimental one as possible.

Prior to Rietveld, structure determination from XRPD data was difficult because of the overlap in peaks that tends to occur in the 1-dimensional data space. Rietveld's method is important in that it finds a way of modelling the XRPD pattern by looking at individual contributions to the diffraction envelope at any point along the 2θ axis. By doing this it is possible to work with individual overlapping peaks.

Rietveld refinement uses a least squares minimisation on the following function:

$$WSS = \sum w_i (I_i^{\exp} - I_i^{calc})^2, \, w_i = \frac{1}{I_i^{\exp}} \tag{2.42}$$

where I^{calc} is given by the classical intensity equation:

$$I_i^{calc} = S_F \sum_{j=1}^{Nphases} \frac{f_j}{V_j^2} \sum_{k=1}^{Npeaks} L_k \left| F_{k,j} \right|^2 S_j (2\theta_i - 2\theta_{k,j}) P_{k,j} A_j + bkg_i \tag{2.43}$$

The wave envelope is determined by a range of factors. The material under analysis has contributions due to cell size, space group, atom positions, texture, stress and strain. The sample in the diffractometer will affect the wasve envelope due to its position, shape and orientation. The diffractometer itself has a contribution, due to beam intensity, Lorentz Polarisation, background and radiation. The important point to note is that each of these contributing factors can be expressed mathematically and can be refined.

2.3.5.2 Factors contributing to the wave envelope

The refineable factors are identified below in the intensity equation.

Multiplicity

Multiplicity

$$I_i^{calc} = S_F \sum_{j=1}^{Nphases} \frac{f_j}{V_j^2} \sum_{k=1}^{Npeaks} L_k \left\| F_{k,j} \right\|^2 S_j \left(2\theta_i - 2\theta_{k,j} \right) P_{k,j} A_j + bkg_i$$

Scale factor   Structure factor   Profile shape function   Texture   Background

Lorentz Polarisation factor   Absorption

For each phase present in the sample, the scale factor, S_j, is given by:

$$S_j = S_F \cdot \frac{f_j}{V_j^2} \tag{2.44}$$

where S_F is the beam intensity

f_j is the phase volume fraction

V_j is the phase cell volume.

The Lorentz Polarisation factor, L_K, is a function of the diffractometer and is dependent upon the instrument geometry, the monochromator, the detector, the beam and sample size, and the sample orientation. For Bragg-Brentano geometry, the factor is given by:

$$L_p = \frac{1 + P_h \cos^2(2\theta)}{2(1 + P_h)\sin^2\theta \cos\theta} \tag{2.45}$$

where $P_h = \cos^2(2\alpha)$, a property of the monochromator.

A typical profile for this factor is shown in figure 2.23.

Figure 2.23 Lorentz Polarisation factor profile. Image from

http://pd.chem.ucl.ac.uk/pdnn/diff2/loren.htm

The structure factor is given by:

$$\left|F_{k,j}\right|^2 = m_k \left|\sum_{n=1}^{N} f_n e^{-B_n \frac{\sin^2\theta}{\lambda^2}} (e^{2\pi i(hx_n+ky_n+lz_n)})\right|^2 \tag{2.46}$$

where m_k represents the multiplicity of the k reflection,

N the number of atoms,

B_n the temperature (Debye-Waller) factor,

x_n, y_n, z_n the coordinates of the nth atom,

and f_n the atomic scattering factor.

The X-ray atomic scattering factor, f_n, is proportional to the number of electrons and decreases with 2θ.

Rietveld assumes a Gaussian shape for each peak in the diffraction envelope. For a Gaussian distribution, peak width is given by:

$$H_k^2 = U \tan^2\theta_k + V \tan\theta_k + W \tag{2.47}$$

where U, V and W are the half width parameters,

and θ_k is the centre of the peak.

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To incorporate preferred orientation, $P_{k,j}$, Rietveld employs the March-Dollase formula:

$$P_{k,j} = \frac{1}{m_k} \sum_{n=1}^{m_k} \left(P^2_{MD} \cos^2 \alpha_n + \frac{\sin^2 \alpha_n}{P_{MD}} \right)^{-\frac{3}{2}}$$

(2.48)

where P_{MD} is the March-Dollase parameter,

α_n is the angle between the scattering vector and the crystallographic plane *hkl*.

Again, summation is made over all equivalent *hkl* reflections, m_k.

For Bragg-Brentano geometry involving a thick sample, the absorption factor, A_j, is given by:

$$A_j = \frac{1}{2\mu}$$

(2.49)

where μ is the linear absorption coefficient of the sample. For a thin sample the absorption depends upon 2θ, as detailed in 2.2.4.3.

The background term, bkg_i, is a polynomial function in 2θ, given by:

$$bkg(2\theta_i) = \sum_{n=0}^{N_b} a_n (2\theta_i)^n$$

(2.50)

where N_b is the polynomial degree,

a_n the polynomial coefficient.

2.3.5.3 Least squares parameters

Rietveld defines two lists of parameters for use in the least squares process. The first list contains the profile parameters. These give the the positions, the halfwidths and the asymmetry of the Bragg peaks, plus the preferred orientation. These parameters are:

U, V, W   half width parameters

Z   zero point

A, B, C, D, E, F   unit cell parameters

P	asymmetry parameter
G	preferred orientation parameter

His second list contains what he calls structural parameters. These relate to the cell contents:

c	scale factor, such that $y_{calc} = c.y_{obs}$
Q	overall isotropic temperature parameter
x_i, y_i, z_i	fractional coordinates of ith atom
B_i	atomic isotropic temperature parameter
n_i	occupation number

2.3.5.4 Measuring the quality of the refinement

Least squares refinement can be measured in a number of ways. Rietveld refinement minimises the weighted sum of the squares (equation 2.42):

$$WSS = \sum w_i (I_i^{exp} - I_i^{calc})^2, w_i = \frac{1}{I_i^{exp}}$$

A common measure for the quality of refinement is the weighted R profile:

$$R_{wp} = \sqrt{\frac{\sum_{i=1}^{N} \left[w_i (I_i^{exp} - I_i^{calc}) \right]^2}{\sum_{i=1}^{N} \left[w_i I_i^{exp} \right]^2}}, w_i = \frac{1}{\sqrt{I_i^{exp}}} \qquad (2.51)$$

Rietveld states that a computer program based on his method allows the refinement or otherwise of any parameter in the least square process. This is essentially the same process used today in programs such as GSAS (Larson and Von Dreele 1994), which will be discussed further in chapter 5. An image showing this program in operation is given is figure 2.24.
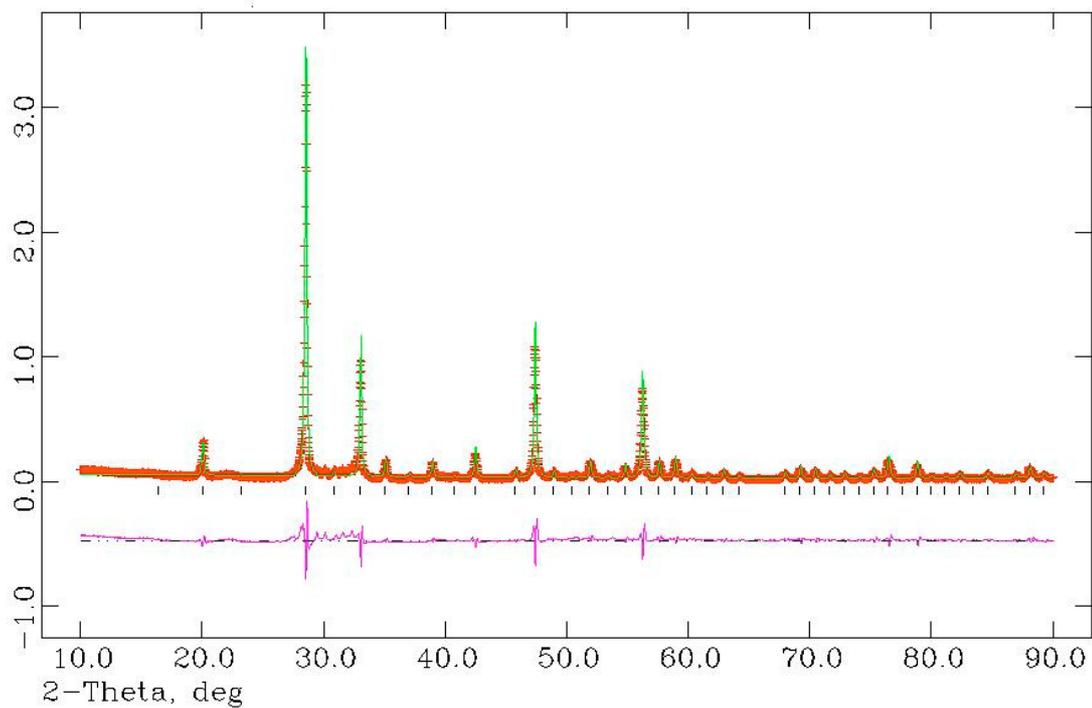
Figure 2.24 Full profile refinement of an XRPD pattern using the program GSAS.

Figure 2.24 shows the experimental data as a series of horizontal ticks marking the wave envelope. The calculated pattern follows the same profile but as a solid line. The difference between the two histograms is shown by the lower line. The peak positions are shown by vertical ticks.

3 DIFFERENTIAL SCANNING CALORIMETRY

3.1 INTRODUCTION

Differential Scanning Calorimetry (DSC) is a thermal analysis technique used primarily to investigate enthalpy changes, such as those associated with change of phase, crystallisation or chemical reactions. It is defined by the ASTM as '*a technique in which the difference in energy input into a substance and a reference material is measured as a function of temperature, while the substance and reference material are subjected to a controlled temperature program*' (ASTM).

There are typically two types of DSC program: isothermal hold and temperature ramp. During an isothermal hold the sample is heated to a defined temperature and held there for a certain period of time. A temperature ramp involves heating the sample across a temperature range at a defined rate. In both situations, the purpose of the experiment is to follow a physical change in the sample by observing its absorption or release of heat.

All the DSC experiments in this thesis involved temperature ramps. When a material is heated there is generally a correlation between heat input and temperature. That is, with continued heating the material increases in temperature. However, at certain points where events such as phase changes exist, there occur anomalies in the DSC output. These thermal events involve additional heat either being taken in or given out by the material, as the structure rearranges in some manner. At some temperature, the material starts to undergo a chemical or physical transformation that involves the release or absorption of heat and no further change in temperature is seen until the reaction has completed. The ordinate value in the DSC output at any given time or temperature is related to the difference in heat flow between a reference sample and the material under analysis.

3.2 INSTRUMENTATION

Both sample and reference are held in small pans, often made from alumina. In some cases the reference may just be an empty pan, which was the experimental set up

employed during this work. It is important that the specific heat capacities of the pans are as close as possible; generally this means that pans of identical size and material are used. If a reference sample is used in the reference pan then it is also important that it is of a similar mass to the sample material. Both pans are equipped with a thermocouple for determination of temperature, and a heating element. The pans may be blanketed with a chosen gas during the experimental run. Typically the sample and reference are heated slowly through a pre-determined temperature range. When the sample undergoes a physical change, which may be endothermic or exothermic, the device measures the heat input or output difference which then arises between the sample and the reference. The electrical input to the sample pan is then adjusted to bring the temperatures in line. This input, which is measured in mW, is convertible into the amount of heat needed to keep the sample and reference at the same temperature. Therefore the DSC effectively measures the heat involved in the transition.

The heater connected to the reference pan supplies power at the pre-determined rate, heating the reference in a linear manner according to the experiment in progress. The sample heater adjusts in proportion to the temperature difference between the two pans. The difference in the power consumption of the 2 heaters is amplified and plotted as a function of temperature.

It is important to note that the alumina pans themselves will have their own contribution to the signal and therefore their effect is measured via a preliminary run with both pans empty, using the same conditions (heaing rate, gas atmosphere and flow). The resulting signal can then be subtracted from the experimental signal to determine the contribution from the sample alone.

A schematic of a DSC is shown in figure 3.1.
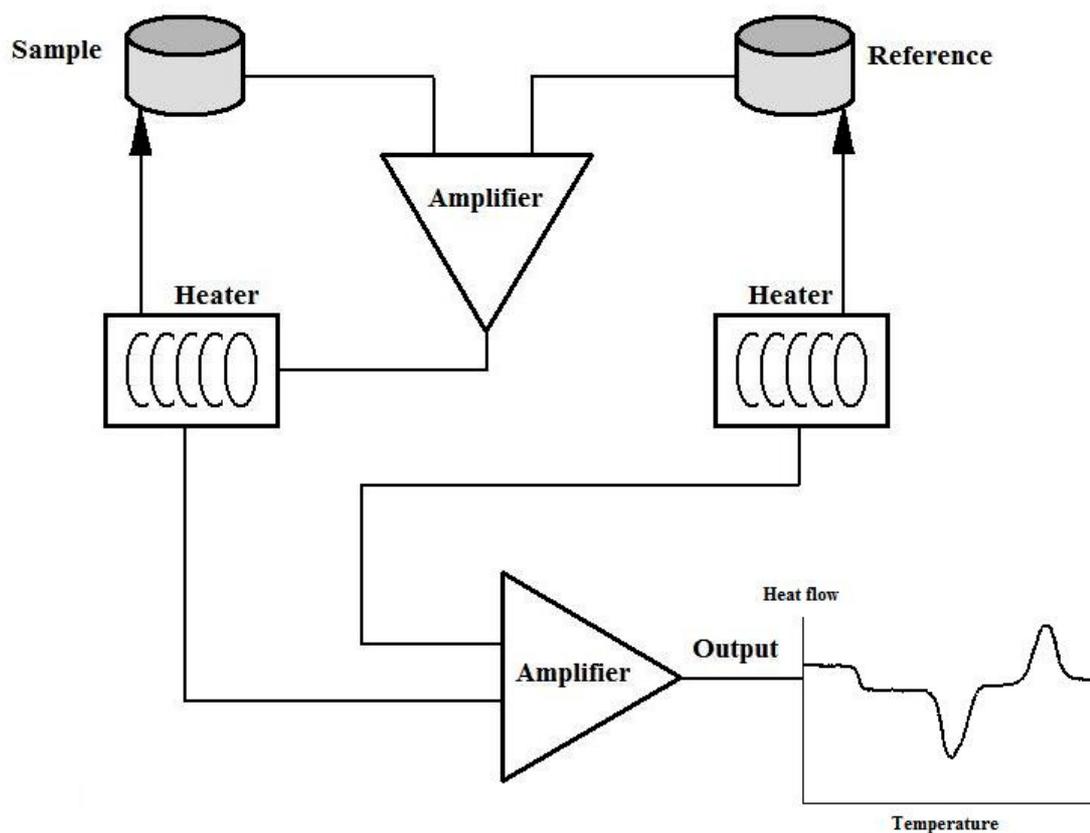
Figure 3.1 DSC schematic.

Figure 3.2 shows the instrument used in this work, a Netszch ST449 F3 Jupiter. This instrument is capable of heating a sample up to 1500°C. It is also capable of weighing the sample throughout the run, allowing a TG (thermogravimetric) analysis of the reaction. The base unit (below) and the hoisting device/furnace (above) can be clearly seen. The sample carrier is the thin white alumina rod between the two, upon which sit the sample and reference pans.
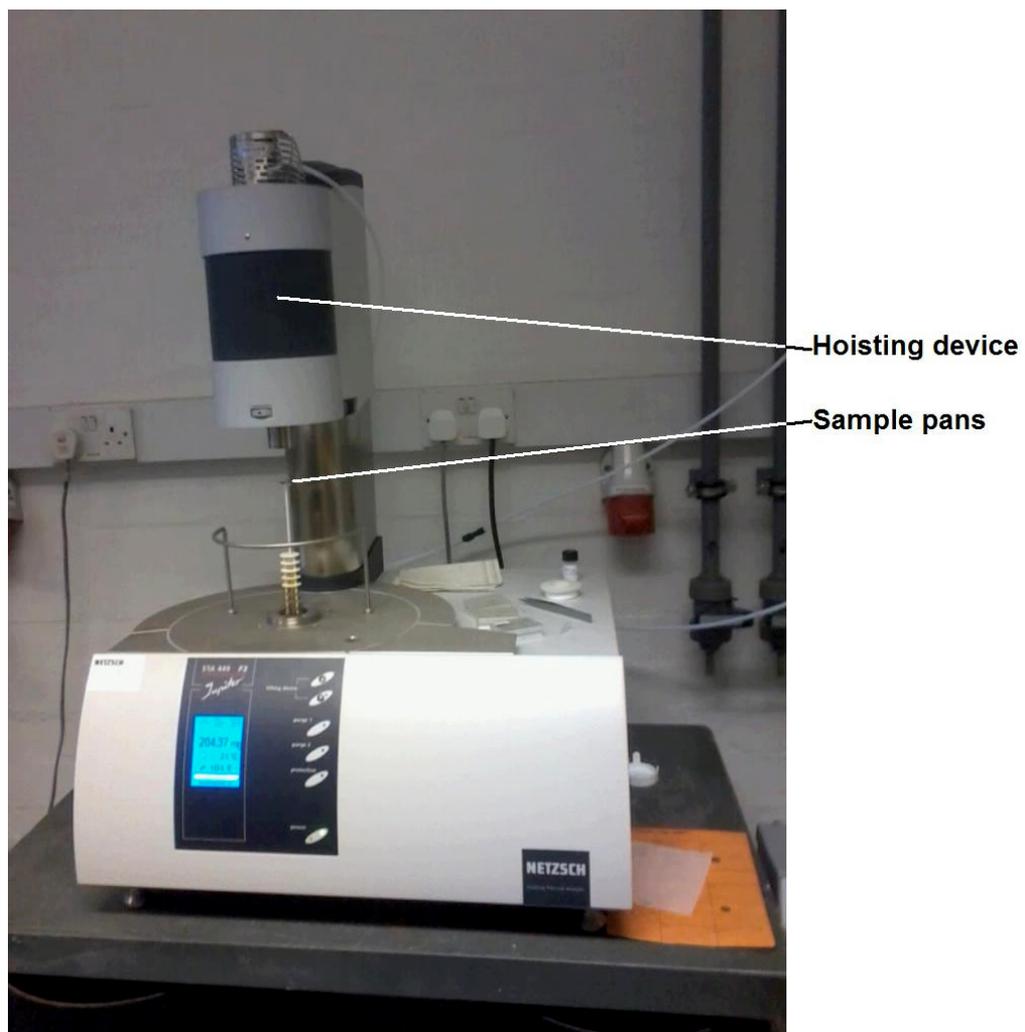
Figure 3.2 Netzsch ST449 F3 Jupiter DSC.

Figure 3.3 shows the two alumina pans. The pan nearer the camera is the one containing the sample, which in this case is the pale green powder of Pr_2O_3.
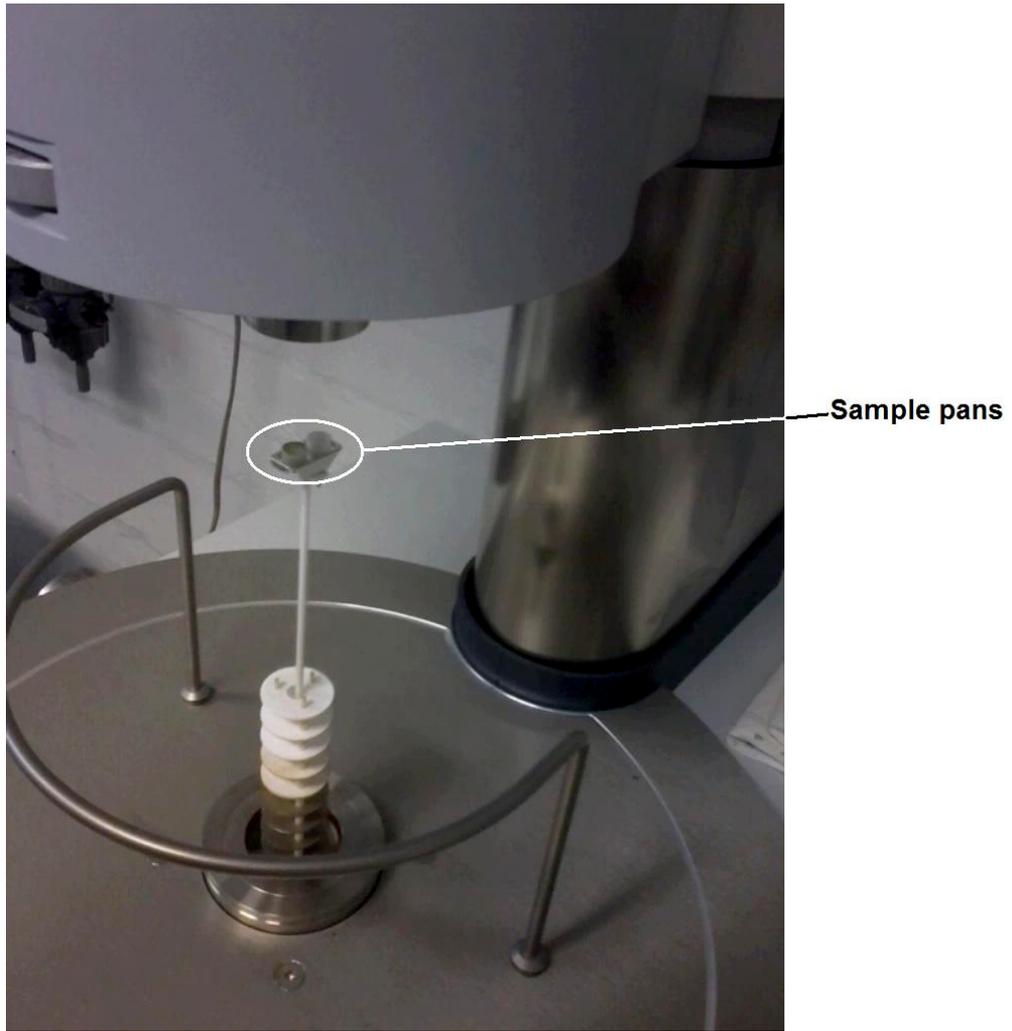
Figure 3.3 Sample carrier with reference and sample pans atop.

Figure 3.4 shows a cut-away schematic of the instrument.
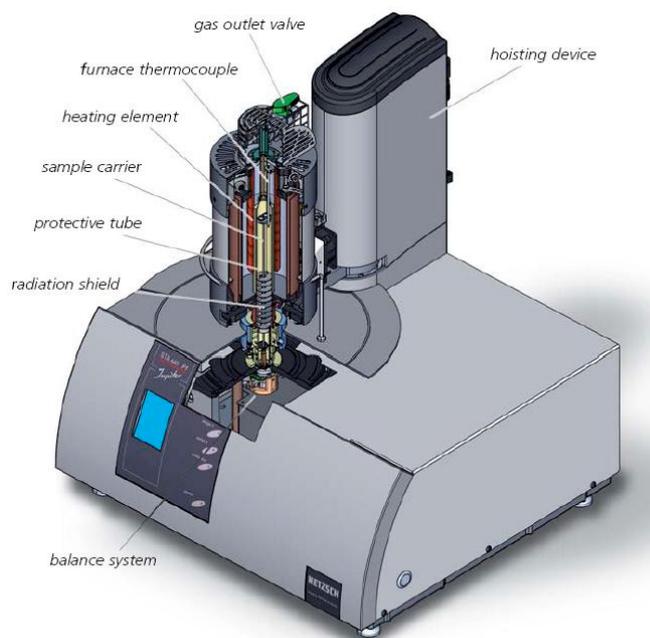
Figure 3.4 Cut-away schematic of the DSC. Image taken from NETZSCH manual (NETZSCH).

The base unit of the instrument contains the connections for the thermocouples and the gas flow. Gas is introduced from a cylinder beside the instrument, although it is possible to run the machine without any carrier/protective gas. The sample carrier is plugged into a socket and can therefore be easily exchanged. The experimental setup, data acquisition and analysis are performed by an associated computer running NETZSCH software.

3.3 INSTRUMENTAL OUTPUT

The data from the instrument can give a number of pieces of information. The shape of the curve at the transition temperature indicates the nature of the reaction e.g. a sharp peak may imply it occurs suddenly; a broad peak may indicate that an increasing energy input is needed to convert the material across the ramp. Integration of the area under the heat flow curve yields the enthalpy change associated with the thermal event. The shift in position of the transition over ramps of different rates can be used to determine the activation energy.
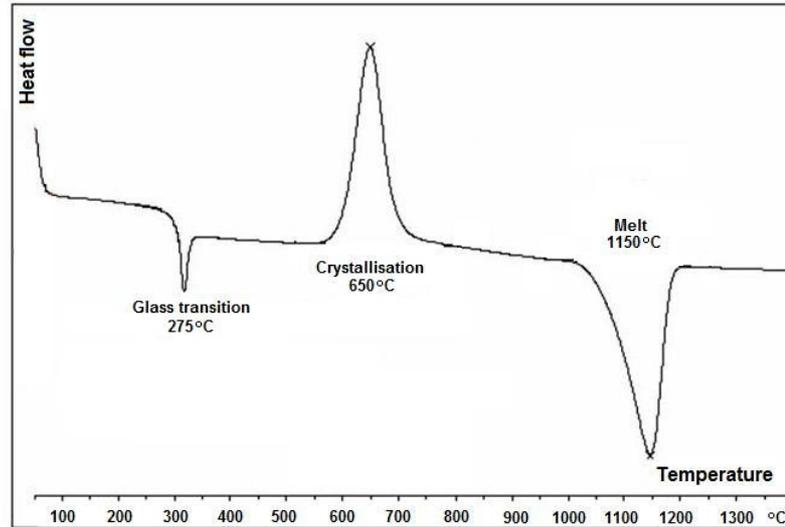
Figure 3.5 DSC curve showing heat flow against temperature (exothermic is 'up').

Figure 3.5 shows typical features associated with a typical DSC curve. The glass transition at low temperature represents a shift in structure from amorphous to some degree of short range order. Once a glass transition has taken place the level of the trace is taken as the new baseline. Crystallisation is an exothermic process, whereby a system attains a greater stability by the release of heat. It is represented by a negative peak in the trace i.e. $\Delta\dfrac{dH}{dt}$ is negative. Melting is an endothermic process, whereby heat is taken in to the sample, represented by a positive peak i.e. $\Delta\dfrac{dH}{dt}$ is positive. The area between a particular peak and the baseline represents the enthalpy change giving rise to it, assuming the heat capacity of the reference is unchanging across the peak.

$$\int \left(\frac{dH}{dt} \right)_{sample} dt = \Delta H_{sample} \qquad (3.1)$$

As the DSC is held at constant pressure, the measured heat flow is proportionate to the enthalpy change:

$$\left(\frac{dq}{dt}\right)_P = \frac{dH}{dt} \qquad (3.2)$$

The heat flow difference between the pans is given by:

$$\Delta\frac{dH}{dt} = \left(\frac{dH}{dt}\right)_{sample} - \left(\frac{dH}{dt}\right)_{reference} \qquad (3.3)$$

Heat capacity for a transition, C_p, can be determined from the baseline shift and is given by:

$$C_p = \left(\frac{dq}{dT}\right)_P = \left(\frac{dH}{dT}\right)_P \qquad (3.4)$$

Using the chain rule:

$$C_p = \left(\frac{dH}{dt}\right)\cdot\left(\frac{dt}{dT}\right) \qquad (3.5)$$

$\frac{dH}{dt}$ represents the baseline shift, $\frac{dt}{dT}$ is the inverse of the scan rate of the machine.

By finding the area under the curve it is possible to make use of the following relationship:

$$\Delta H = kA \qquad (3.6)$$

where ΔH is the enthalpy change

k is the calorimetric constant, which is particular to the machine used

A is the area under the curve

The equilibrium constant k and the standard enthalpy change for the process, ΔH^{Θ}, can be found from the van't Hoff equation:

$$\Delta H^{\ominus} = RT^2 \left(\frac{d \ln k}{dT} \right) \tag{3.7}$$

the standard free energy change from:

$$\Delta G^{\ominus} = -RT \ln k \tag{3.8}$$

the standard entropy change from:

$$\Delta S^{\ominus} = \Delta H^{\ominus} - T \Delta S^{\ominus} \tag{3.9}$$

The instrument has particular limitations, which need to be borne in mind. A high sample mass increases the signal strength, but can reduce resolution if there are overlapping peaks. The greater the heating rate, the greater is the signal strength, but as with sample mass, there is a trade-off with peak resolution. If a gas is used, one with high thermal conductivity, such as helium, causes lower signal strength but better peak separation. Additionally, there is a limit to the heating rate that can be employed to prolong longevity of the furnace. Typically a rate no greater than 20K/min is used with this instrument, as in the figure below.
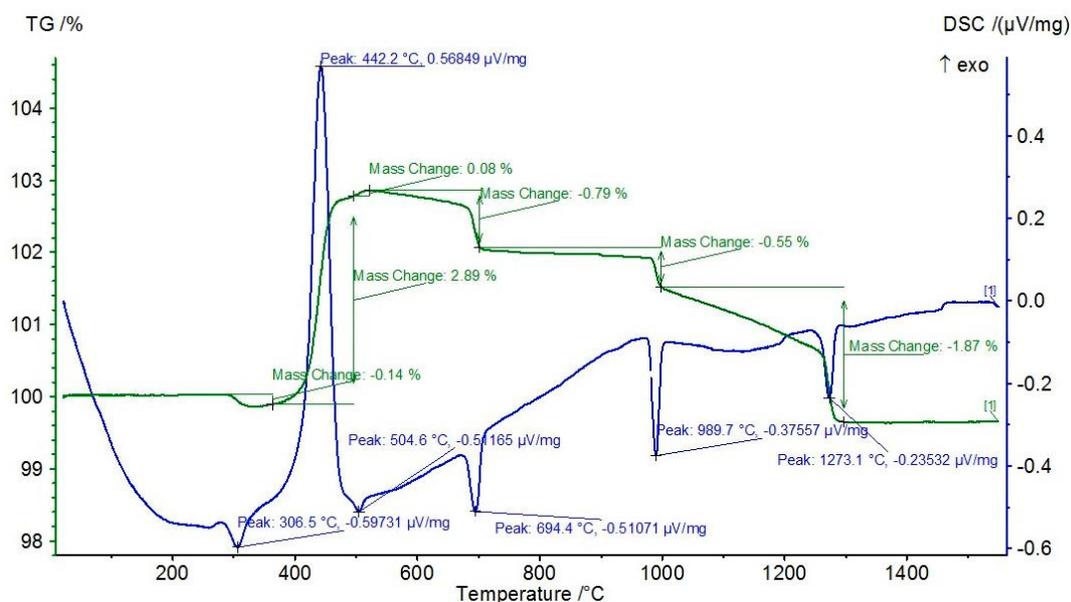
Figure 3.6 20K/min ramp for praseodymium sesquioxide.

As an example of the information that can be obtained, figure 3.6 shows a combined DSC-TG plot for the praseodymium-oxygen system over the temperature range 20°C to 1550°C. As indicated in Chapter 1, the system is rich in that it shows a large number of stoichiometries, each existing in its own temperature range. The lower line, showing sharps peaks, represents the DSC and shows that, for example, a significant thermal event occurs at 442°C, with an accompanying mass increase of 2.83% shown by the TG plot (upper line). A small endotherm at about 500°C is associated with a further but small mass increase. Following this, there are three more endotherms, each associated with a mass loss. More detailed analyses of the DSC-TG plots obtained will be presented in Chapter 8.

4 REACTION KINETICS

4.1 INTRODUCTION

The purpose of any kinetic study is to record how a reaction progresses with time under certain environmental conditions. To do this, it is necessary to establish how much conversion from reactant to product has taken place at any moment. By creating a mathematical model for the reaction, the rate constant at any temperature can be derived and subsequently used to derive the activation energy for the process.

The fundamental aims of a kinetic model are to:

(1) visualise how the transformation arises and propagates;

(2) express the degree of conversion as a function of time;

(3) determine the rate constants and activation energy.

In this study the work has been concerned with conversion against temperature only. Data used in the analyses were obtained from both XRPD and DSC. Three models have been used to determine the rate constants activation energies, namely the Shrinking Sphere Model, the JMAK model and Kissinger Analysis.

4.2 PHASE BOUNDARIES

As a general rule, the heavier is the lanthanoid under investigation, the more effort is required to induce a particular phase change. Figure 1.5 shows the C → B phase boundary to be an upwardly sloping line. That is, the transition temperature increases with the atomic number of the lanthanoid. Consequently, the heating temperature and/or heating time required to convert a particular low temperature phase to a high temperature one for a specific lanthanoid sesquioxide will increase with the atomic weight of the lanthanoid. For example, the C → B transition in europia is easily achieved by heating to 1300ºC for one hour. However, heating the C form of gadolinia to even 1500ºC for an hour produces little change. It is only when the oxide is kept at this temperature for an extended period that the transition occurs. Gadolinium is the adjacent element to europium and yet the change in kinetics is considerable. We would

therefore expect that for the heaviest oxides the heating times would be considerably extended and the product materials would show less metastability on quenching.

4.3 DATA USED IN KINETIC MODELLING

4.3.1 Data from XRPD

As one phase converts to another there is an associated change in peak intensities within the XRPD pattern. The peaks for the reactant phase will fall in height as the peaks for the product emerge from the baseline. A method of measuring the degree of conversion at any point is to select a prominent Bragg reflection arising from the reactant phase. For the lanthanoid sesquioxides, the most comprehensive historic study (Stecura 1966) looked at the change in intensity of the 222 Bragg reflection in the reactant phase. In my work this was identified at 2θ of 28.45º for Eu_2O_3 and 29.65º for Yb_2O_3. An alternative method would be to look for the peaks arising from the product phase. Two prominent peaks in the monoclinic phase are the 401 and 11-2 reflections. These occur at 2θ of 29.3º and 32.3º for Eu_2O_3 and 30.15º and 33.7º for Yb_2O_3. However, it would be more practical to use the 222 reflection in the reactant phase. Firstly, the maximum intensity is known from the start and so any decrease in the peak (and associated increase in the peak of the high-temperature modification) can be immediately ascribed a fractional conversion. With the product phase, the final heights of the new peaks are not known at the start of the experiment. Secondly, the 222 peak is readily discernible in the reactant pattern whereas the emerging peaks in the product pattern will not be so in the initial stages.

Figure 4.1 shows a series of XRPD patterns taken over time, clearly showing a reactant peak at 40.2° of 2θ falling in intensity. What is not as clear is the magnitude of the corresponding rise in the product peak at 38.1°.
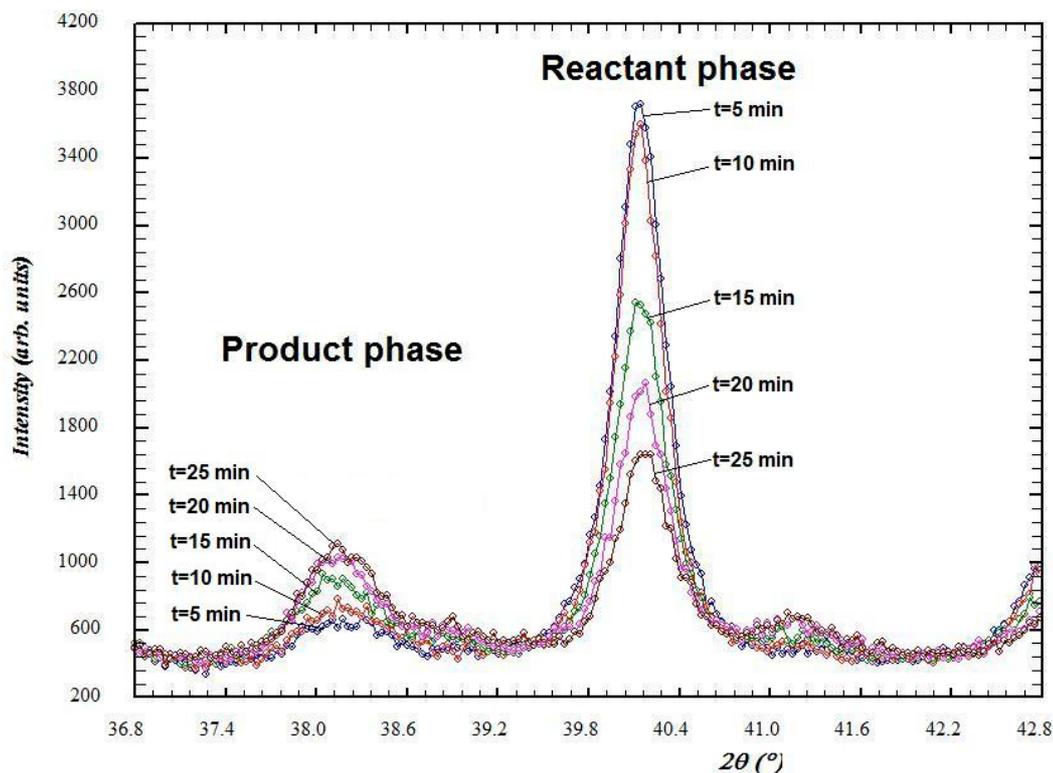
Figure 4.1 Changes in peak intensity over time.

4.3.2 Data from DSC

The data used from the DSC work are the heating rate and the temperature of onset of conversion. For each material the approximate temperature at which the product starts to convert to reactant is determined by a wide range temperature ramp. Once this conversion point has been established, a number of temperature ramps up to the conversion temperature are carried out, each at a different heating rate. The onset temperature is known to vary with the heating rate (generally a slower heating rate has a lower conversion temperature). A process called Kissinger Analysis (Kissinger 1955) can then be applied to this information to determine the rate constant and activation energy.

4.4 SHRINKING SPHERE MODEL

A model historically adopted for kinetic work in the solid state is based on a shrinking sphere model (Tammann 1925), (Jander 1927). This model states that the nucleating

sites of the new phase are created quickly in comparison to their propagation throughout the bulk material. This means the growth of the phase boundary is the rate-determining factor. Tamman postulated that the rate of increase of the high-temperature phase at the phase boundary was inversely proportional to time.

$$\frac{dy}{dt} = \frac{k_T}{t} \tag{4.1}$$

where y is the thickness of high-temperature phase layer, t is time and k_T is a constant.

On integration this becomes:

$$y = k_T \ln t + A_1 \tag{4.2}$$

where A_1 is a constant of integration.

Jander noted that some phase reactions did not agree with Tamman's postulate. He found that for some reactions it was the square of the thickness of the product layer that was proportional to time.

$$y^2 = 2k_j t \tag{4.3}$$

This is an integrated form of $\dfrac{dy}{dt} = \dfrac{k_j}{y}$

This equation states that the rate of growth is inversely proportional to the thickness at time t. In this situation the existence of product slows the reaction as it progresses. This equation is known as Jander's law. It is one of three possible reactions in the solid state.

The second type of reaction occurs if the phase boundary moves at a constant rate:

$$\frac{dy}{dt} = k \tag{4.4}$$

Then the product does not influence the rate of reaction. On integration this equation becomes:

$$y = kt + A_2 \qquad (4.5)$$

where A_2 is a constant of integration. However, A_2 is equal to zero because at $t=0$ the thickness of product is also zero.

The third type of reaction is where the rate of reaction is proportional to the thickness of product i.e. it is catalysed by the thickness of product. It is given by:

$$\frac{dy}{dt} = k_A y \qquad (4.6)$$

On integration this becomes:

$$\ln y = k_A t = A_3 \qquad (4.7)$$

where A_3 is a constant of integration, again equal to zero.

Both Stecura and Ainscough employed Jander's second equation in relation to the rare earth sesquioxides. However, before the equation can be used it is necessary to ascertain the degree of conversion to the high-temperature modification.

Assuming the reactant particles are spherical, an increase in the product thickness results in a decrease in the radius, r, of the reactant particle, to $r-y$. The density of the reactant particle prior to reaction is:

$$\rho_A = \frac{M_1}{V_1} \qquad (4.8)$$

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where ρ_A is the density, M_1 is the mass of the reactant particle and V_1 is the volume of the reactant particle. After reaction, the density of the reactant particle is:

$$\rho_A = \frac{M_2}{V_2} \tag{4.9}$$

where M_2 is the mass of reactant particle at time t and V_2 is the volume of the reactant particle at time t. As the density of the reactant material does not change, equations 4.8 and 4.9 can be equated.

$$\rho_A = \frac{M_1}{V_1} = \frac{M_2}{V_2} \tag{4.10}$$

Rearranging:

$$\frac{1}{V_1} = \frac{M_2}{M_1.V_2} \tag{4.11}$$

If α is the fraction of the particle which has reacted then $(1-\alpha)$ represents M_2/M_1. Substituting $(1-\alpha)$ into equation 4.11 gives:

$$\frac{1}{V_1} = \frac{1-\alpha}{V_2} \tag{4.12}$$

The volume of the reactant particle before reaction is $\frac{4}{3}\pi r^3$ and its volume after time t is $\frac{4}{3}\pi(r-y)^3$. Substituting into equation 4.12 gives:

$$(1-\alpha).\frac{4}{3}\pi r^3 = \frac{4}{3}\pi(r-y)^3 \tag{4.13}$$

Rearranging:

$$r - y = r(1 - \alpha)^{\frac{1}{3}} \tag{4.14}$$

Expressing as y, the thickness of the product layer, gives

$$y = r(1 - (1 - \alpha)^{\frac{1}{3}}) \tag{4.15}$$

Equating this with equation 4.5:

$$kt = r(1 - (1 - \alpha)^{\frac{1}{3}}) \tag{4.16}$$

where k is the linear rate of propagation.

Rearranging:

$$(1 - \alpha) = \left(1 - \frac{kt}{r}\right)^3 \tag{4.17}$$

Expanding the polynomial and keeping only the first term:

$$1 - \alpha = e^{\frac{-3kt}{r}} \tag{4.18}$$

Rearranging:

$$\ln\left(\frac{1}{1 - \alpha}\right) = kt \tag{4.19}$$

where k is the rate constant. This is the equation presented by Stecura. Ainscough uses the equivalent:

$$-\ln(1 - x) = kt \tag{4.20}$$

where $x = \alpha$. This is a first order rate equation. A plot of $-\ln(1 - \alpha)$ against t should yield a straight line with gradient k. Therefore for any set of isotherms the rate constant

at that temperature can be determined. The activation energy can then be determined by use of the Arrhenius equation:

$$k = Ae^{\frac{-EA}{RT}}$$

(4.21)

where k is the rate constant, A is a constant, E_A is the activation energy, R is the gas constant and T is the temperature. The Arrhenius equation can be rewritten as:

$$\ln k = \ln A - \frac{E_A}{RT}$$

(4.22)

A plot of $\ln k$ against $\frac{1}{T}$ should yield a straight line with gradient $\frac{-E_A}{R}$. Therefore the activation energy for a particular phase transformation may be determined.

4.5 THE JMAK MODEL

The Johnson-Mehl-Avrami-Kolmogorov (JMAK) model comes from work carried out during the late 1930s and early 1940s. The equations involved are often referred to as Avrami equations; Avrami published extensively during this period, in a series of papers in the Journal of Chemical Physics, all of which are still referenced today whenever the model is discussed (Avrami 1939, 1940, 1941).

The model assumes that the new phase is created from randomly-distributed germ nuclei already existing in the reactant phase. If there is no further nucleation during the reaction i.e. all nuclei are present at the start, the material is termed *site saturated*. With increasing temperature some of these germ nuclei become growth nuclei, creating grains in the product phase. These grains grow at a linear rate. As the reaction progresses the degree of transformation follows a sigmoidal or S-type curve. That is, conversion is initially slow but increases exponentially. There comes a point of inflexion in the curve, which represents a running out of space in the product phase, where grains are impinging on one another. The curve then decreases in gradient until it

flattens out. A typical sigmoidal curve is shown in red in figure 4.2. The sigmoidal curve is typical of many processes in nature involving growth.
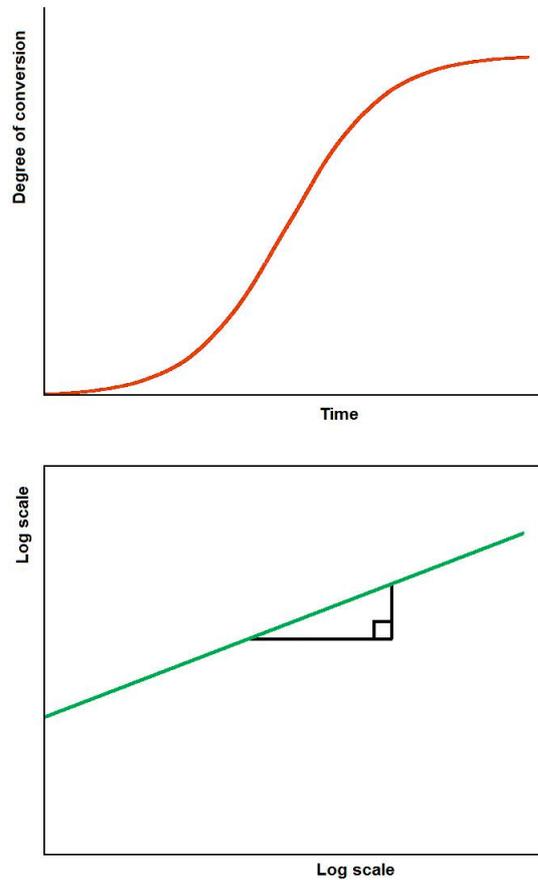
Figure 4.2 Sigmoidal function (top) and its linearised form.

The basic sigmoid curve, called the logistic curve, is given by:

$$P(t) = \frac{1}{1 + e^{-t}} \qquad (4.23)$$

where P is the population and t is time. This basic relationship, or variations upon it, is used in many fields, including biology, economics and artificial neural networks. Its basic feature is that for small values of t growth appears exponential and there is an equilibrium point at which it begins to slow.

The fundamental principle in the derivation of the JMAK equation is to express the change in fractional volume of product relative to the existing fractional volume. The fractional volume changed to product is given by:

$$f = \frac{V}{V_{total}} \tag{4.24}$$

where f is the fraction changed, V is the volume of product and V_{total} is the total volume of the reaction space (reactant plus product). As the reaction progresses, germ nuclei grow into grains of the new phase. Eventually some of these grains impinge on one another, as shown in figure 4.3.

A Nucleation

B Growth
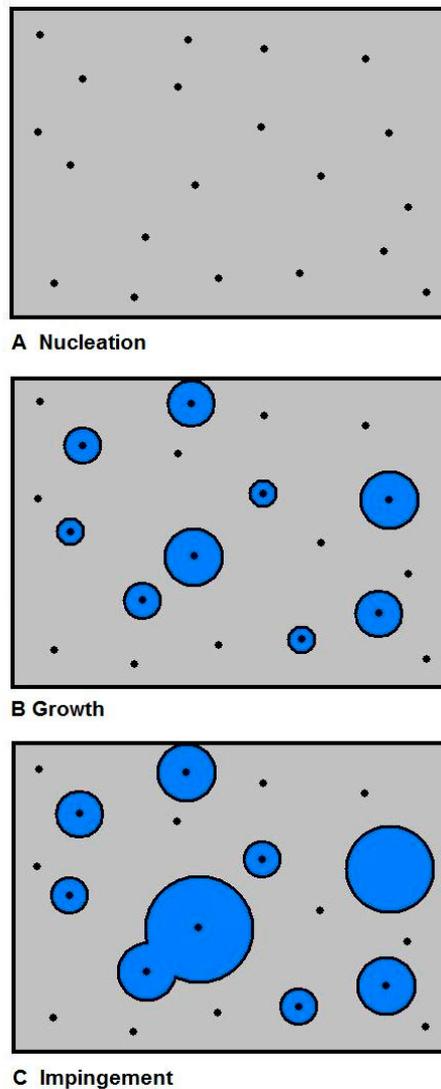
C Impingement

Figure 4.3 Germ nucleation, grain growth and grain impingement.

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Avrami appreciated that as grains grow they eventually come into contact with one another (figure 4.3C) and growth would cease. He therefore defined an extended volume fraction, as if the grains always had free reactant space in which to grow and no impingement occurs.
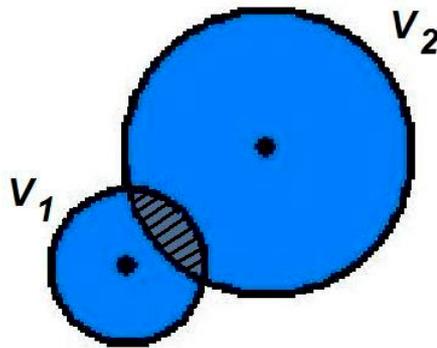
Figure 4.4 Illustration of extended volume.

Figure 4.4 shows an enlarged region of figure 4.3C where 2 grains have grown against one another. The volume of the smaller grain is given by V_1 and that of the larger grain by V_2. The fraction changed by virtue of the extended volume is given by:

$$f_{ext} = \frac{V_1 + V_2}{V_{total}}$$

(4.25)

The actual fraction changed is given by:

$$f = \frac{V_1 \cup V_2}{V_{total}}$$

(4.26)

where $\cup$ represents the union of the two circles i.e. the area of both but including their overlap just once. The relationship between increments in f and f_{ext} can be expressed by the following differential equation:

$$df = df_{ext}(1 - f)$$

(4.27)

As is typical of any growth, the amount of material already transformed, f, acts as a feedback in the above equation, limiting the change possible at any moment by the volume already transformed. At reaction completion, the volume of a grain transformed is given by:

$$V = \frac{4}{3}\pi r^3 \qquad (4.28)$$

where r is the radius of the grain, assuming a spherical reaction volume. The radius r can be expressed as a distance st where s is the radial speed of propagation of the grain surface and t is time. Therefore:

$$V = \frac{4}{3}\pi(st)^3 \qquad (4.29)$$

Multiplying the volume of the grain by N, the density of nuclei, gives the extended volume:

$$f_{ext} = \frac{4}{3}\pi N(st)^3 \qquad (4.30)$$

The extended fraction increment, df_{ext}, is given by:

$$df_{ext} = 4\pi N s^3 t^2 \,.dt \qquad (4.31)$$

Substituting into equation 4.27:

$$df = 4\pi N s^3 t^2 \,.dt \,(1\text{-}f) \qquad (4.32)$$

Rearranging:

$$\frac{df}{1-f} = 4\pi N s^3 t^2 .dt \qquad (4.33)$$

A constant k is defined, which contains the nucleation and growth terms:

$$k = \frac{4}{3}\pi N s^3$$ (4.34)

Recognising that $\frac{d}{dx}\left(\frac{1}{x}\right) = \ln x$:

$$-\ln(1 - f) = kt^3$$ (4.35)

Rearranging:

$$f = 1 - e^{-kt^3}$$ (4.36)

This is the specific Avrami equation for site saturated growth in three dimensions. The general form is given by:

$$f = 1 - e^{-kt^n}$$ (4.37)

Whereas the value of k is determined by energy-dependent terms, the value of n, called the Avrami exponent, is interpreted as defining the geometry of the transformation. Generally the number of dimensions involved in the growth is equal to n, although it is quite possible to have fractional values for n. Therefore it is not always straightforward to deduce the geometry from the value. For any reaction, the value of n should be a constant irrespective of temperature. Typical values for n are given in table 4.1.

Value of n	Geometry	Type of growth
$1 < n < 2$	1D	Needle
$2 < n < 3$	2D	Platelet
$3 < n < 4$	3D	Spherical – all nucleation sites present from start
4	3D	Spherical – nucleation occurs throughout, slowing to zero

Table 4.1 Values of the Avrami exponent, n, and corresponding geometries.

The more familiar form of the JMAK equation is the linear form, resulting from taking the double logarithm of the general equation. It is given by:

$$\ln(-\ln(1 - f)) = \ln k + n\ln t \tag{4.38}$$

or

$$\ln\left(\ln\left(\frac{1}{1-f}\right)\right) = \ln k + n\ln t \tag{4.39}$$

Thus a plot of $\ln(-\ln(1 - f))$ against $\ln t$ should yield a straight line with intercept $\ln k$ and gradient n. In practice it is possible to use a variety of quantities to calculate the value of f. If the fractional conversion is inferred by the change in peak intensity in an XRPD pattern, the following relationship can be used:

$$\ln\left(\ln\left(\frac{1}{1-I_t}\right)\right) = \ln k + n\ln t \tag{4.40}$$

where I_t is the intensity arising from a selected peak of the new phase. Alternatively, this could be determined from the decrease in the intensity of a selected peak in the reactant phase. For example, if the intensity had fallen to 90% of its original value, the intensity I_t attributable to the product phase would be taken to be 0.1.

As with a Shrinking Sphere Model, the activation energy can then be determined by use of the Arrhenius equation (equation 4.22). Again, a plot of $\ln k$ against $\frac{1}{T}$ should yield a straight line with gradient $\frac{-E_A}{R}$.

4.6 KISSINGER ANALYSIS

Kissinger noted that the temperature of maximum deflection during a DSC analysis varied with temperature. This variation is determined by the activation energy. By

linearising a function relating heating rate and temperature it is possible to derive the activation energy. Kissinger started with a generic equation describing a solid → solid + gas reaction process:

$$\frac{dx}{dt} = A(1-x)^n . e^{\frac{-E_A}{RT}} \tag{4.41}$$

where x is the fraction converted, $\frac{dx}{dt}$ is the reaction rate, n is the reaction order, R is the gas constant, E_A is the activation energy and T is the temperature. When the reaction rate is at a maximum, $\frac{d^2x}{dt^2}$ is equal to zero. Solving the above equation for $\frac{d^2x}{dt^2}$

$$\frac{d^2x}{dt^2} = \frac{dx}{dt} \left[\frac{E_A}{RT^2} . \frac{dT}{dt} - An(1-x)^{n-1} . e^{\frac{-E_A}{RT}} \right] \tag{4.42}$$

Substituting φ for the heating rate, $\frac{dT}{dt}$

$$\frac{d^2x}{dt^2} = \frac{dx}{dt} \left[\frac{E_A}{RT^2} . \varphi - An(1-x)^{n-1} . e^{\frac{-E_A}{RT}} \right] \tag{4.43}$$

The expression $n(1-x)^{n-1}$ approximates to 1, therefore:

$$\frac{d^2x}{dt^2} = \frac{dx}{dt} \left[\frac{E_A}{RT^2} . \varphi - Ae^{\frac{-E_A}{RT}} \right] \tag{4.44}$$

Equating this with zero gives:

$$\frac{E_A}{RT^2} . \varphi = Ae^{\frac{-E_A}{RT}} \tag{4.45}$$

Differentiating:

$$\frac{d\left(\ln\dfrac{\varphi}{T_m{}^2}\right)}{d\left(\dfrac{1}{T_m}\right)} = \frac{-E_A}{R} \tag{4.46}$$

Therefore a plot of $\ln\dfrac{\varphi}{T_m{}^2}$ against $\dfrac{1}{T_m}$ should yield a straight line with gradient

$\dfrac{-E_A}{R}$. Once E_A is known, A can be calculated from equation 4.45, above.

An alternative method of calculating the activation energy is by use of the Arrhenius relationship:

$$\frac{1}{\tau} = \frac{1}{\tau_0}\exp\left(-\frac{E_A}{k_B T}\right) \tag{4.47}$$

where $1/\tau$ is the inverse rate constant, k^{-1}, or *time constant*, E_A is the activation energy, k_B is the Boltzman constant and T is the isothermal annealing temperature. The use of this expression assumes that the transformation takes place at a single temperature and in a single step. The expression can also be written as:

$$k(T) = k_0.e^{\frac{-E_A}{k_B T}} \tag{4.48}$$

Both equations can be linearised as:

$$\ln\frac{1}{\tau} = \ln\frac{1}{\tau_0} - \frac{E_A}{k_B T} \tag{4.49}$$

and

$$\ln k(T) = \ln k_0 - \frac{E_A}{k_B T} \tag{4.51}$$

A series of isothermal anneals carried out close to the transition temperature will give a series of values for τ (or k) against T. A plot of $\ln \dfrac{1}{\tau}$ (or $\ln k$) against $\dfrac{1}{k_B T}$ should yield a straight line with gradient $-E_A$.

5 SOFTWARE USED IN THIS WORK

5.1 SOFTWARE FOR XRPD

All the software mentioned in section 5.1 is hosted on the CCP14 (Collaborative Computational Projects 14) website www.ccp14.ac.uk. This is a site dedicated to the promotion of freely available single crystal and powder diffraction software for academic use.

5.1.1 Determining the peak positions, calculating peak area, stacking of patterns – PowderX and WINPLOTR

PowderX (Dong 1998) is a graphical program for XRPD data analysis. Data from the diffractometer in the form of intensities against 2θ is used as the input information. The output from the Siemens D500 diffractometer is in the form of a RAW file, although PowderX accepts a number of formats. This information is plotted in the form of a histogram, an example of which is shown in figure 5.1.
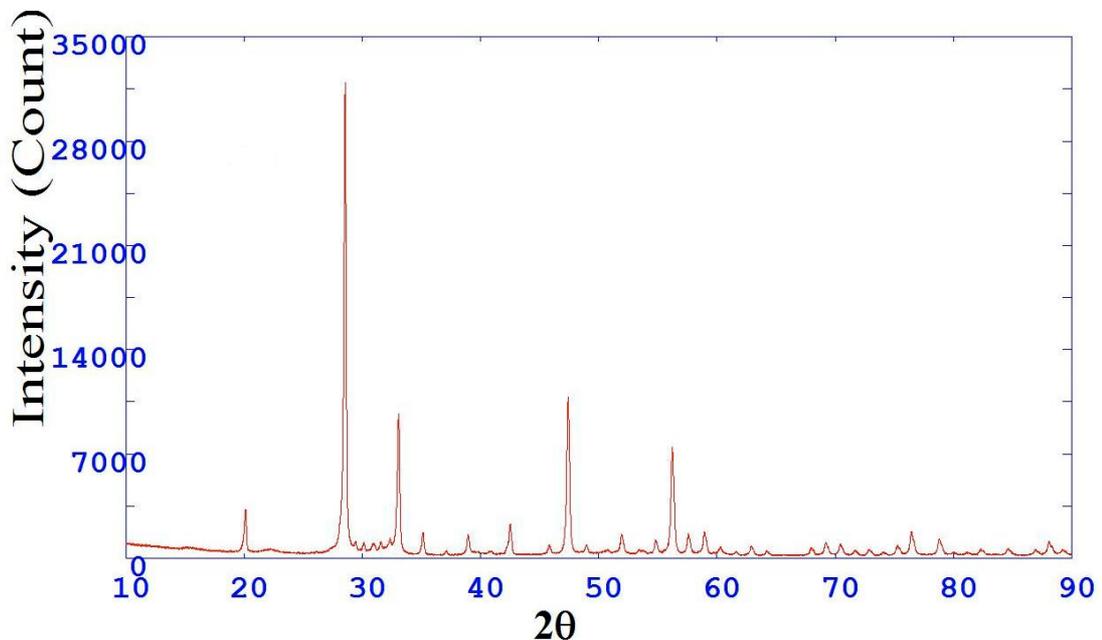
Figure 5.1 Raw data (intensity versus 2θ) displayed in PowderX.

The three functions of PowderX used in this work were:

(i)   removing the part of the histogram attributable to $K\alpha_2$ radiation.

(ii)   removing the background contribution i.e. bringing the Bragg peaks down to the 2θ axis.

(iii)   identification of the peak positions.

Figure 5.2 shows the above histogram after these processes have been applied.
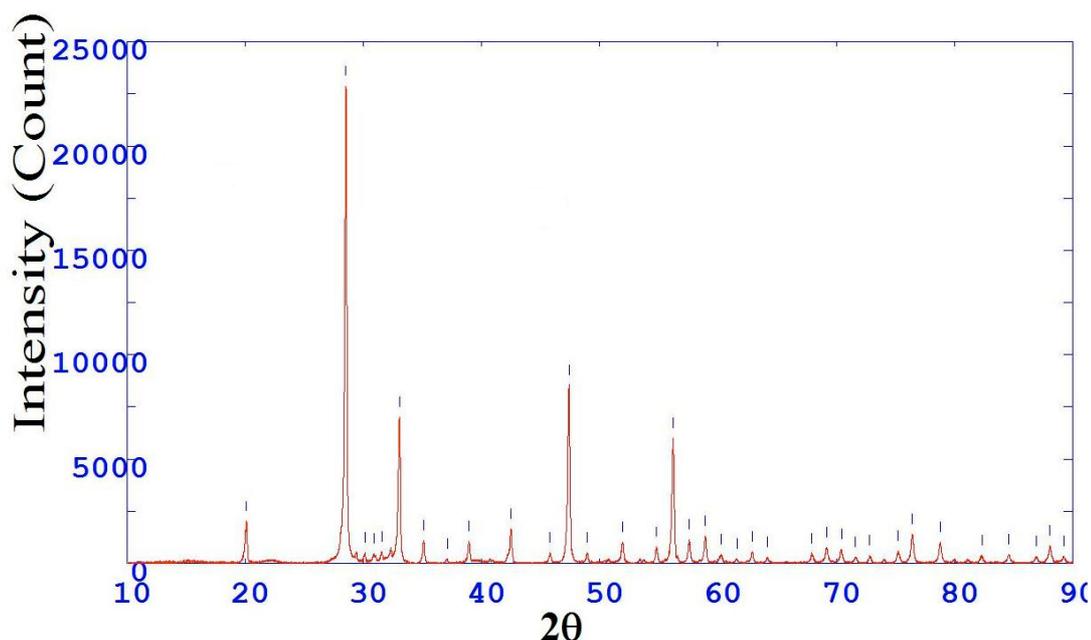
Figure 5.2 Histogram after removal of $K\alpha_2$ contribution, background and identification of peak positions.

A list of the identified line positions can be saved as a text file, ready for use in an indexing program. The adjusted pattern can then be saved in a form for use in the full profile refinement program GSAS.

WINPLOTR (Roisnel and Rodriguez-Carvajal 2010) is another graphical program for analysis of XRPD patterns and comes as part of the Fullprof Suite, written by the same authors. In this work it has been used solely for calculation of peak height/area and for graphically stacking patterns from ramps and anneals.

5.1.2 Indexing – the Crysfire Indexing Suite and GRAPHPRO

The Crysfire Indexing Suite (Shirley 2002) has brought together 10 indexing programs, allowing the user to access them all through a single interface. The peak positions, established above via PowderX, are entered into Crysfire once. Each indexing program can then be applied to the data in turn and will generate a number of possible solutions. As each program generates solutions these are added to a summary file, which, after using all the indexing programs, can be quite extensive. Figure 5.3 shows the input screen of Crysfire where the user enters the peak positions. The screens shot is at the stage of entering the position of the 4th Bragg reflection.

Figure 5.3 Crysfire peak position input screen.

As well as employing the widely used programs ITO, DICVOL and TREOR, Crysfire also contains the programs TAUP (Taupin 1973), KOHL (Kohlbeck and Hörl 1978), FJZN6 (Visser and Shirley 2000), LZON (Shirley *et al* 1978) and LOSHFZRF (Shirley and Louër 1978). An example of a summary file is shown in figure 5.4.

```
Running summary of all solutions logged so far for this dataset name,
sorted in descending order of I20 then Merit (as defined by each program)

I20  Merit    Volume  V/V1 BL IndexProg   Date    Time   Pedig   a       b       c      alpha    beta    gamma    Q(A)
Q(B)      Q(C)      Q(D)      Q(E)     Q(F)  Description (up to 80-chars, from Run-Title line)
20   46.4     740.62  1.00 C ITO12/log   1Feb09 00:51:01   121   8.8750  15.3629  5.4319  90.000  90.000  90.000  126.959
42.370  338.919    .000      .000     .000  EU2O3JAN =
20   45.5     122.56   .17 P ITO12/log   1Feb09 00:51:01   451   5.5902   6.4836  3.5596 102.112 100.931  79.739  338.971
254.118  846.770  169.048  169.562  -84.587 EU2O3JAN =
20   27.0     270.41   .37 P ITO12/log   1Feb09 00:51:01   252   5.4924   7.8532  6.4782 101.933  98.469  88.255  338.843
169.388  254.207   84.915   84.615    .000  EU2O3JAN =
20   24.26    131.389  .18 P LZONv6.23b  1Feb09 00:54:08  20001  5.4791   7.6726  3.1579  90.000  98.219  90.000  340.0557
169.8715 1023.7090  .0000  168.6950   .0000 EU2O3JAN =
20   23.51    159.302  .22 P TAUPv3.3a   1Feb09 00:50:22 Ort__2  3.8332   5.4246  7.6613  90.000  90.000  90.000  680.5873
339.8376 170.3730   .0000    .0000    .0000 EU2O3JAN =
20   23.19    525.194  .71 A KOHLv7.01b  1Feb09 00:52:19    21   7.6749  21.6772  3.1568  90.000  90.000  90.000  169.7677
21.2810 1003.4890   .0000    .0000    .0000 EU2O3JAN =
20   23.03    159.304  .22 P TAUPv3.3a   1Feb09 01:12:42 Ort__2  3.8332   5.4246  7.6613  90.000  90.000  90.000  680.5851
339.8326 170.3722   .0000    .0000    .0000 EU2O3JAN =
20   22.81    218.653  .30 P LZONv6.23b  1Feb09 01:17:11  30691  4.4413  12.5758  3.9599  94.308  97.183  87.264  515.7905
63.6856  651.0135  28.4179 141.3173 -14.0478 EU2O3JAN =
20   22.8     305.18   .41 I ITO12/log   1Feb09 01:13:02   253   4.8405  12.6586  5.1331  97.745 101.707  88.433  445.121
63.561   402.842   42.250  170.337    .000  EU2O3JAN =
20   22.57    215.399  .29 P LZONv6.23b  1Feb09 01:17:11  31120  5.4834  12.7354  3.1667  95.982  98.291  81.027  346.7514
63.6380 1025.5360  42.7164 155.3261 -42.5480 EU2O3JAN =
20   22.16    422.377  .57 F LZONv6.23b  1Feb09 01:17:11  31031 10.0563  13.0082  3.3548  94.198  92.741 104.686  106.1777
63.6534  897.5526  42.2181  42.4850  42.4234 EU2O3JAN =
20   20.82    159.135  .21 P LZONv6.23b  1Feb09 00:54:08  20002  5.4240   7.6675  3.8264  90.000  90.000  90.000  339.9084
170.0934 683.0010   .0000    .0000    .0000 EU2O3JAN =
20   20.5     270.31   .36 P ITO12/log   1Feb09 00:51:01   251   5.4919   7.8530  6.4769 101.936  98.469  88.255  338.905
169.400  254.314   84.954   84.644    .000  EU2O3JAN =
20   20.40    261.038  .35 P LZONv6.23b  1Feb09 01:17:11  31147  5.4293  12.7281  3.8357  95.737  89.967  98.165  346.2968
```

Figure 5.4 Summary file of indexing results.

Figure 5.4 shows a set of results from Crysfire, listed in order of merit. As an example, the best fit to the experimental data is the top entry, with a figure of merit of 46.4. This set of unit cell parameters has enabled the indexing of all the first 20 lines in the pattern, shown by the value of I(20) = 20. The unit cell for this trial structure is orthorhombic (a = 8.875Å, b = 15.3629Å, c = 5.4319Å). Many trial structures may be generated from a diffraction pattern and it is quite possible that the actual solution is not allocated the top position in the summary file, if it is found at all. The user is able to change the tolerance in 2θ i.e. to adjust how far from the actual peak positions the calculated positions are allowed to stray. In some cases increasing this tolerance may bring the actual solution into the summary list if it wasn't already present, but this is at the expense of accepting poor data from the diffractometer. The indexing process is often regarded as the most difficult stage in the process of structure solution. This is because just a small error in measuring the peak positions can generate many unnecessary trial cells, even missing the actual cell altogether. The process of identifying potential cells from the summary list is often one of trial and error. The need for accurately measuring the Bragg reflections and assigning the peak positions is clear.

Although only used in this work when Crysfire failed, GRAPHPRO is a program written by myself for quickly indexing cubic cells.

5.1.3 Space group determination - CHEKCELL

CHEKCELL (Laugier and Bochu) is a program for both manually and automatically finding the best unit cell parameters and space group for the unit cell and has been designed to work in tandem with Crysfire. The peak positions and possible cells are taken from the relevant Crysfire files. An example is shown in figure 5.5.
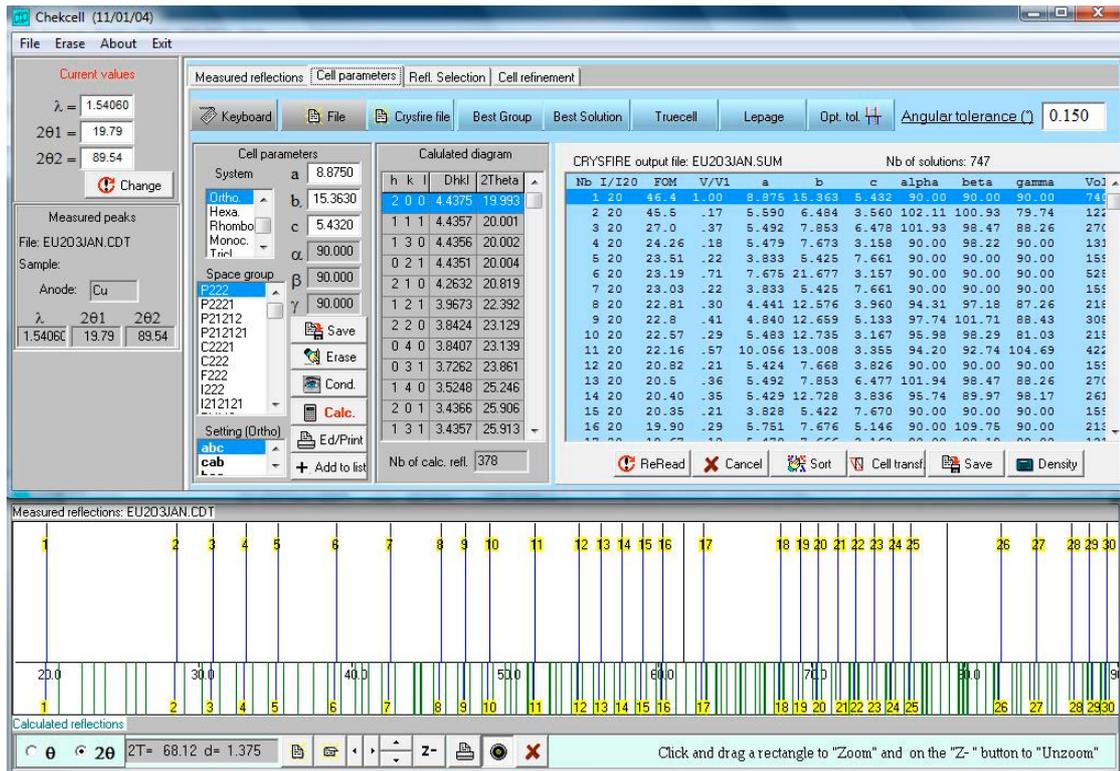
Figure 5.5 CHEKCELL main screen showing trial cells (top half) and comparison of measured and calculated peak positions (bottom half).

Each possible cell, together with the space groups available for it, is used to generate Bragg peak positions. From all the trial cells used, the best fit to the experimental data is taken as a possible solution for the cell (see figure 5.6). It is then possible to refine the trial unit cell parameters to get a better fit to the measured peak positions (see figure 5.7). This is the trial cell to be used in Rietveld refinement.
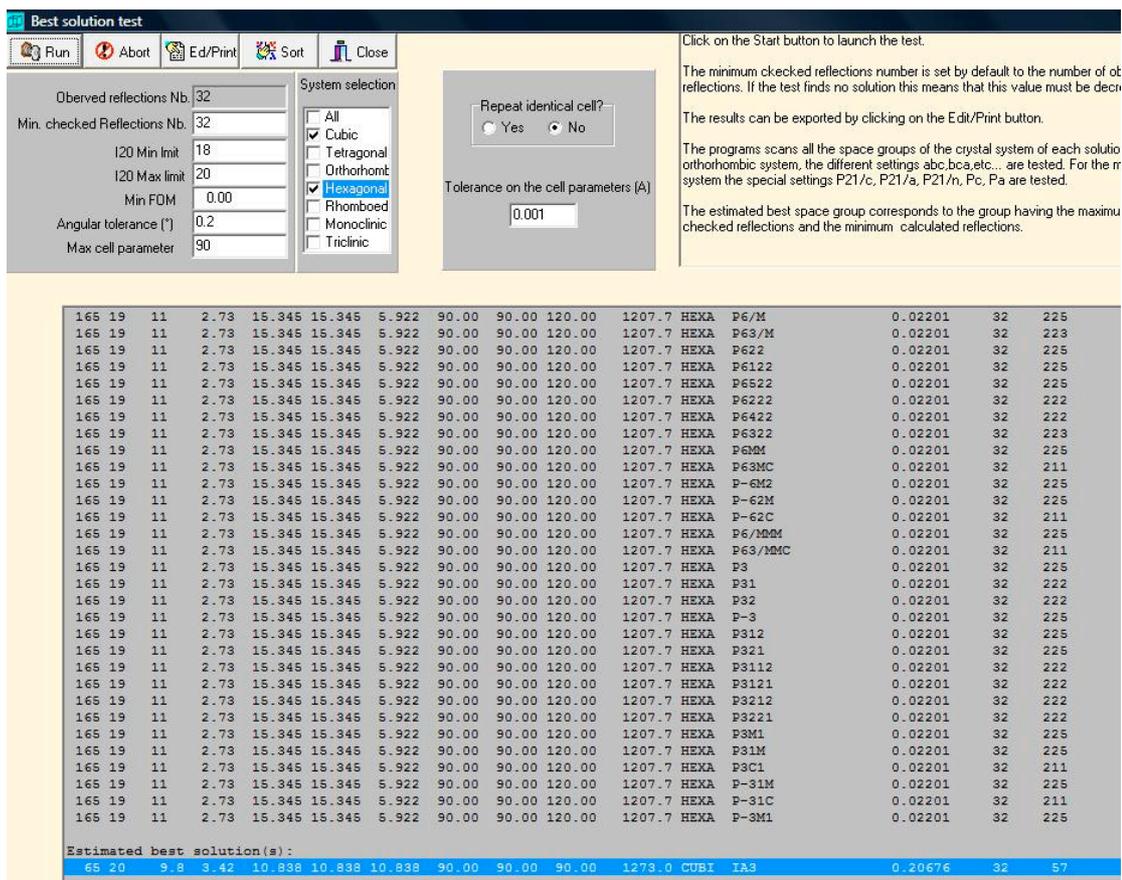
Figure 5.6 Best solution from CHEKCELL (highlighted at the foot of the image).
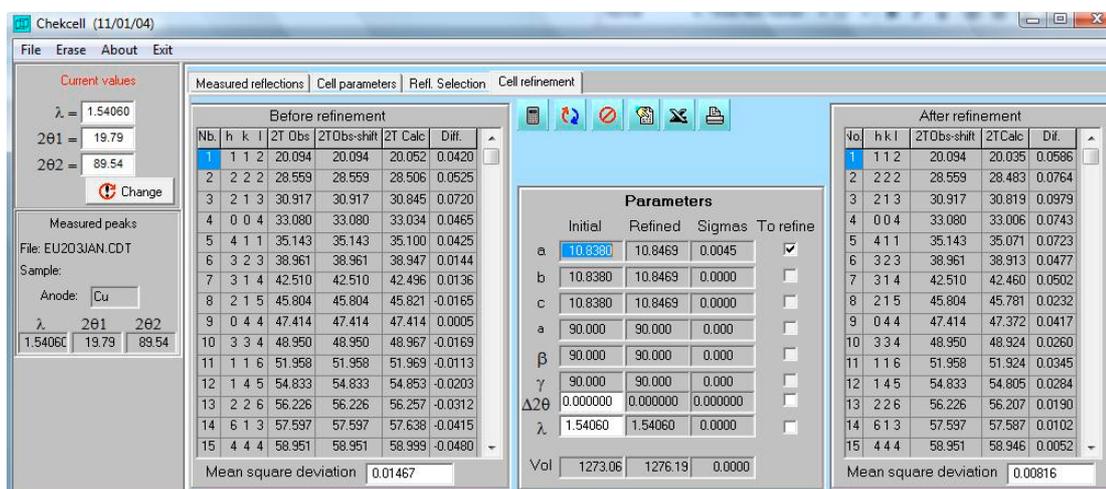
Figure 5.7 Unit cell refinement in CHEKCELL (mean square deviation for the refined

unit cell parameters is lower than initial parameters).

5.1.4 Full profile refinement – GSAS

GSAS (General Structure Analysis System) (Larson and Von Dreele 1994) is a program for performing Rietveld refinement on XRPD data. GSAS itself is a DOS environment application but a graphical user interface, EXPGUI, has recently been developed to assist in its use (Toby 2001). The essential factor with use of full profile refinement is that a close fit to the structure has already been found, which should prevent the program from becoming trapped in local minima. GSAS allows for refinement of the parameters discussed in chapter 2, namely the unit cell parameters, the atomic positions, peak asymmetry, peak profile, preferred orientation and temperature factors. At each stage of refinement a comparison between the experimental and calculated XRPD patterns is made by means of a difference line and a measure of fitness. Ideally only a few parameters should be refined at a time. GSAS is not an automated program and relies on some expertise on behalf of the user. This involves a visual inspection of the two patterns at each stage. For example, if all the peaks are displaced by the same amount there may be a zero error adjustment. If the 2 patterns are slightly out of scale the unit cell parameters may need refining. If the peak heights do not quite match then the atom positions can be adjusted. Asymmetry in the measured peaks can be modelled by adjusting the peak profile parameters. Figure 5.8 shows an example of a pattern where a close match has been achieved using GSAS.
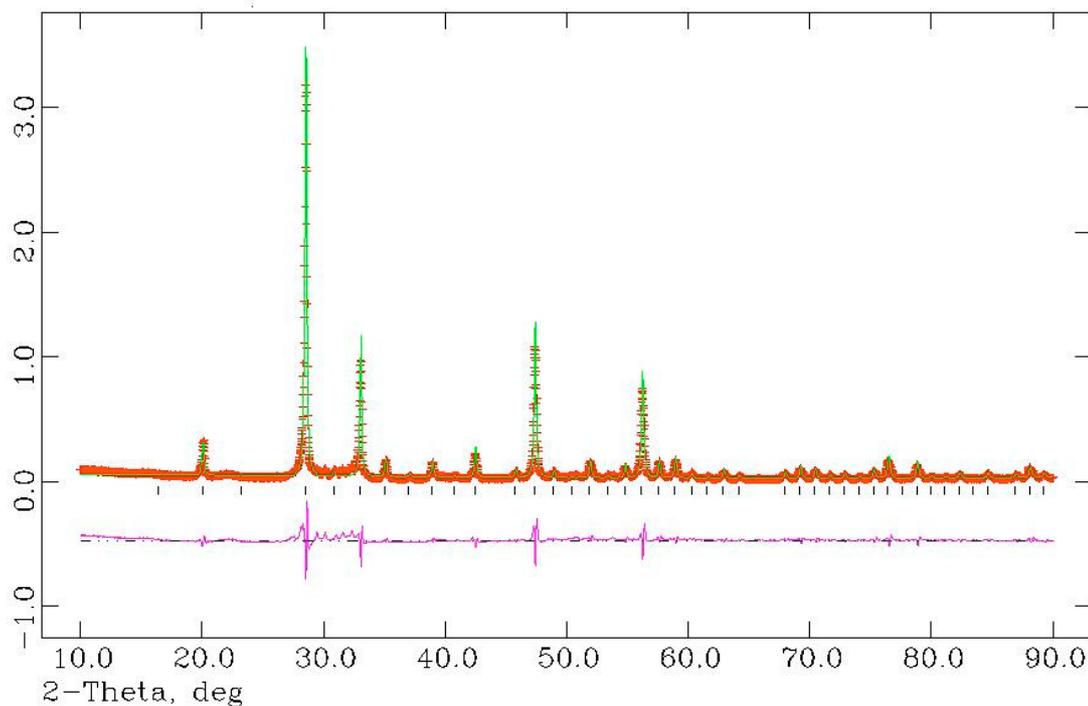
Figure 5.8 Histogram after refinement in GSAS.

Lines represent data as follows: experimental data is the series of horizontal ticks marking the wave envelope. Calculated pattern follows the same profile but as a solid line. Difference plot is shown by the lower line. Peak positions are shown by vertical tick marks. Intensity is in arbitrary units.

The full crystal structure obtained from GSAS, consisting of the unit cell parameters, atom positions, occupancies and thermal parameters can then be put into a standard crystal structure file format such as CIF or SHELXL. This can then be used in crystal structure plotting software, examples of which are given in figures 7.15 to 7.17.

5.2 SOFTWARE FOR DSC-TG

The Netzsch DSC is supplied with software for both recording and analysing data from the machine. The recording software allows input of sample information including identity and weight. It is also possible to use the in-built balance to weigh the sample. An instruction file can then be written which creates a heating programme for the machine.

The Netzsch software was used predominantly for identification of transition temperatures and mass changes due to oxidation and reduction. A typical example of the screen display is shown in figure 5.9.
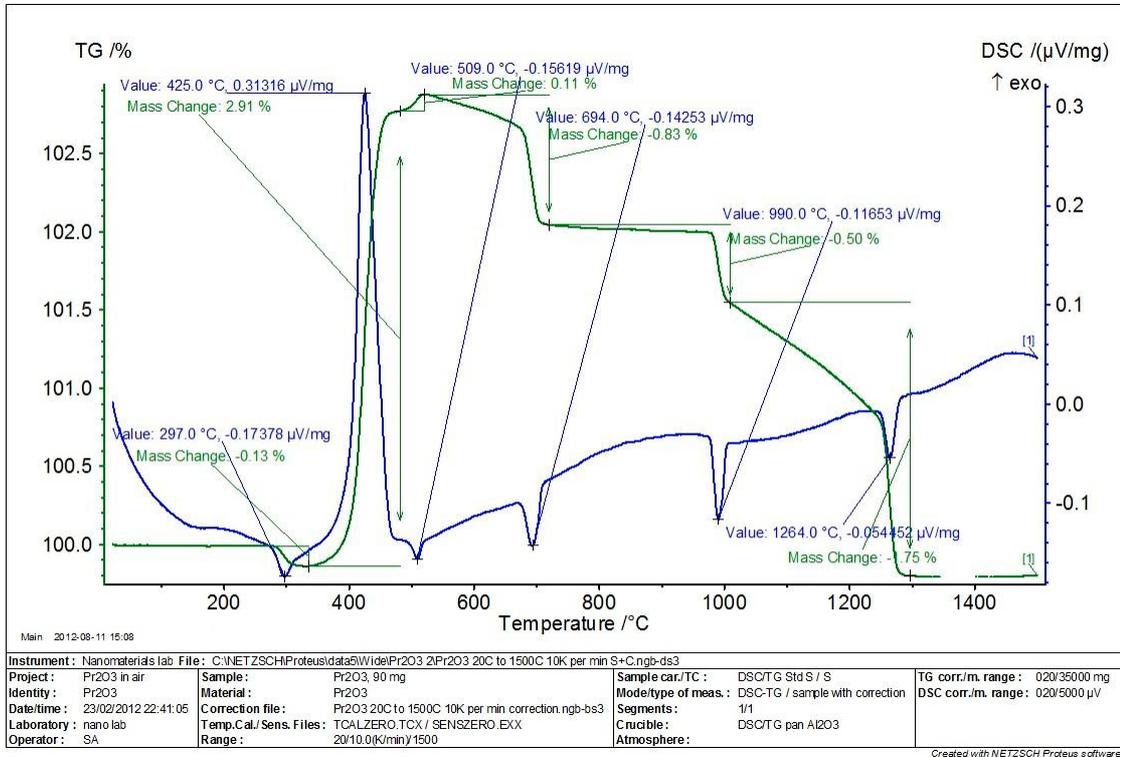
Figure 5.9 Combined DSG-TG plot. DSC plot shows sharp peaks; TG mass changes are highlighted..

From the image it is evident that the thermal events shown by the deflections in the DSC plot are all accompanied by changes in the weight of the sample. The sample represented is a metal oxide and the weight changes all show either oxidation or reduction.

6 SAMPLE PREPARATION AND EXPERIMENTAL CONDITIONS

This chapter contains all the experimental details for the work carried out in this thesis. The work consisted of three areas: ambient temperature XRPD on commercially-obtained samples and on the same samples following annealing; in-situ high-temperature XRPD; and DSC-TG. The work was carried out with the intention of demonstrating phase changes and determining kinetic data.

6.1 AMBIENT TEMPERATURE XRPD

Samples of polycrystalline material were obtained as follows:

Material (sample number in parentheses)	Supplier
(1) Eu_2O_3	Alfa Aesar
(2) Gd_2O_3	Alfa Aesar
(3) Yb_2O_3	Alfa Aesar
(4) Pr_2O_3	Sigma-Aldrich
(5) Tb_2O_3	Sigma-Aldrich
(6) Pr_2O_3	Alfa Aesar
(7) Yb_2O_3	Alfa Aesar
(8) Gd_2O_3	Apollo
(9) Nd_2O_3	Alfa Aesar
(10) Sm_2O_3	Alfa Aesar
(11) Eu_2O_3	Alfa Aesar

Table 6.1 Samples obtained for XRPD and DSC-TG.

6.1.1 Preliminary XRPD patterns on untreated samples

Each of the samples (1) to (5) and (9) to (11) was thoroughly ground with a pestle and mortar and XRPD data recorded using Cu Kα radiation according to the following table.

Sample	Diffractometer	Range	Step	Time	Standard
(1) Eu_2O_3	Siemens D500	10° - 90°	0.01°	12 hours	Quartz
(2) Gd_2O_3	Siemens D500	10° - 90°	0.01°	12 hours	Quartz
(3) Yb_2O_3	Siemens D500	10° - 90°	0.01°	12 hours	Quartz
(4) Pr_2O_3	Bruker D8	10° - 92.43°	0.01°	12 hours	Corundum
(5) Tb_2O_3	Bruker D8	10° - 92.43°	0.01°	12 hours	Corundum
(9) Nd_2O_3	Bruker D8	10° - 92.43°	0.01°	1 hour	Corundum
(10) Sm_2O_3	Bruker D8	10° - 92.43°	0.01°	1 hour	Corundum
(11) Eu_2O_3	Bruker D8	10° - 92.43°	0.01°	1 hour	Corundum

Table 6.2 XRPD schedule for samples.

6.1.2 Sample annealing

Samples were annealed according to table 6.3.

Sample	Furnace	Temperature	Time	Cooling
(1) Eu_2O_3	Carbolite tube	1334ºC	1 hour	Slow cooled
(2) Gd_2O_3	Carbolite tube	1334ºC	1 hour	Slow cooled
(2) Gd_2O_3	Heraeus CL-G77	1500ºC	1 hour	Quenched
(2) Gd_2O_3	Heraeus CL-G77	1500ºC	7 hours	Quenched
(3) Yb_2O_3	Heraeus CL-G77	1500ºC	1 hour	Quenched
(3) Yb_2O_3	Heraeus CL-G77	1500ºC	5 hours	Quenched
(7) Yb_2O_3	Glass furnace	1800ºC	5 hours	Quenched
(8) Gd_2O_3	Netzsch DSC	1500ºC	7 hours	Quenched

Table 6.3 Heating scheme for samples.

6.1.3 Post-annealing XRPD

The annealed samples were reground and powder diffraction patterns taken according to the following table. Sample (8) was mounted on a 0.5mm glass capillary and exposed to 0.827130Å synchrotron radiation. For the remainder of the samples Cu $K\alpha$ radiation was used.

Sample	Anneal	Diffractometer	Range	Step	Time	Standard
(1) Eu_2O_3	1 hour at 1334ºC	Siemens D500	10° - 90°	0.01°	12h	Quartz
(2) Gd_2O_3	1 hour at 1334ºC	Siemens D500	10° - 90°	0.01°	12h	Quartz
(2) Gd_2O_3	1 hour at 1500ºC	Siemens D500	10° - 90°	0.01°	12h	Quartz
(2) Gd_2O_3	7 hours at 1500ºC	Siemens D500	10° - 90°	0.01°	22h	Quartz
(3) Yb_2O_3	1 hour at 1500ºC	Siemens D500	10° - 90°	0.01°	12h	Quartz
(3) Yb_2O_3	5 hours at 1500ºC	Siemens D500	10° - 90°	0.01°	22h	Quartz
(7) Yb_2O_3	5 hours at 1800ºC	Bruker D8	10° - 92.43°	0.01°	12h	Corundum
(8) Gd_2O_3	7 hours at 1500ºC	DLS beamline I11	0° - 149.999°	0.001°	1h	Quartz

Table 6.4 XRPD schedule for annealed samples.

6.2 IN SITU HIGH-TEMPERATURE XRPD

6.2.1 Praseosdymia ramp in air

Sample (4) Pr_2O_3 was mounted in a PANalytical X'Pert diffractometer and XRPD data recorded at ambient temperature for 2θ between 18° and 60° in 0.03° steps. The whole scan took 15 minutes. The sample was then heated in air from 25°C to 800°C and back to 125°C, in 25°C steps. At each temperature an XRPD pattern was recorded from 18° to 60° of 2θ.

6.2.2 Praseodymia isothermal hold in air - phase change at 275ºC

A sample of (4) Pr_2O_3 was mounted in the PANalytical X'Pert diffractometer, held at 230ºC in air and XRPD data recorded every 5 minutes from 18° to 60° of 2θ until the reactant material had converted. The process was repeated for new samples at 240ºC, 250°C, 260°C, 270°C and 280°C.

6.2.3 Praseodymia quench in air

The 280°C sample from 6.2 was quenched to ambient temperature XRPD data recorded from 18° to 60° of 2θ.

6.3 DSC-TG

6.3.1 Praseodymia

6.3.1.1 Wide run in nitrogen

4 Samples of (4) Pr_2O_3 were heated in the Netzsch STA449 F3 DSC using a protective nitrogen gas of 20ml/min and a purge of nitrogen at 60ml/min. The DSC-TG measurements were made from 20^oC to 1550^oC at 10°C/min. The samples used in the third and fourth runs were subject to heating in an attempt to remove any bound gas prior to placing in the DSC, as follows:

Sample	Run	Temperature	Time
(4) Pr_2O_3	3	170°C	10 mins
(4) Pr_2O_3	4	380°C	30 mins

Table 6.5 Pre-DSC-TG heating schedule for sample (4).

6.3.1.2 Wide run in air

2 samples of (6) Pr_2O_3 were heated in the Netzsch STA449 F3 DSC in air. The DSC-TG measurements were made from 20^oC to 1400^oC at 10°C/min.

2 samples of the same material were heated in air from 20°C to 1400°C and back again to look for reversibility of reactions.

6.3.1.3 Ramps in nitrogen

Seven temperature ramps were performed on (4) Pr_2O_3 in nitrogen using a protective nitrogen gas of 20ml/min and a purge of nitrogen at 60ml/min. The DSC-TG measurements were made from 200^oC to 600^oC. The heating rates were 1, 2, 4, 7, 10, 15 and 20°C/min.

6.3.1.4 Ramps in air

Seven temperature ramps were performed on (6) Pr_2O_3 in air. The DSC and TG measurements were made from 200°C to 500°C. The heating rates were 1, 2, 4, 7, 10, 15 and 20°C/min. A second set of ramps on (6) Pr_2O_3 was performed at the above rates, from 20°C to 1500°C.

6.3.1.5 Gas absorption

Sample (6) Pr_2O_3 was left exposed to the atmosphere for an extended time to determine what effect this had on the chemical structure. A DSC-TG measurement was carried out from 20°C to 1500°C at 10°C/min after 7, 78 and 85 days respectively.

6.3.2 Terbia

6.3.2.1 Wide run in nitrogen

2 samples of (5) Tb_2O_3 were heated in the Netzsch STA449 F3 DSC using a protective nitrogen gas of 20ml/min and a purge of nitrogen at 60ml/min. The DSC-TG measurements were made from 20°C to 1550°C at 10°C/min. 1550°C represents the temperature limit of the instrument. The phase diagram indicates a cubic to monoclinic phase transition at about 1600°C. The purpose of this experiment was to determine whether the transition could be induced below this temperature. However, nothing was seen in the DSC data to warrant further mention in the results section. This indicates that the transition is indeed beyond the range of the instrument.

7 RESULTS FROM X-RAY POWDER DIFFRACTION

This chapter contains all the XRPD work carried out on PrO_x, Nd_2O_3, Sm_2O_3, Eu_2O_3, Gd_2O_3 and Yb_2O_3. The work had six aims, namely:

(i) to establish the ambient phase(s);

(ii) to induce phase changes by heating;

(iii) to determine the non-ambient phases either in situ or after quenching;

(iv) to perform kinetic measurements using in situ data;

(v) to match phase changes against the published phase diagrams;

(vi) and to note any discrepancies between this work and the published phase diagrams.

7.1 AMBIENT TEMPERATURE XRPD

7.1.1 Diffraction patterns

The XRPD patterns recorded at ambient temperature are shown in figures 7.1 to 7.13 below.
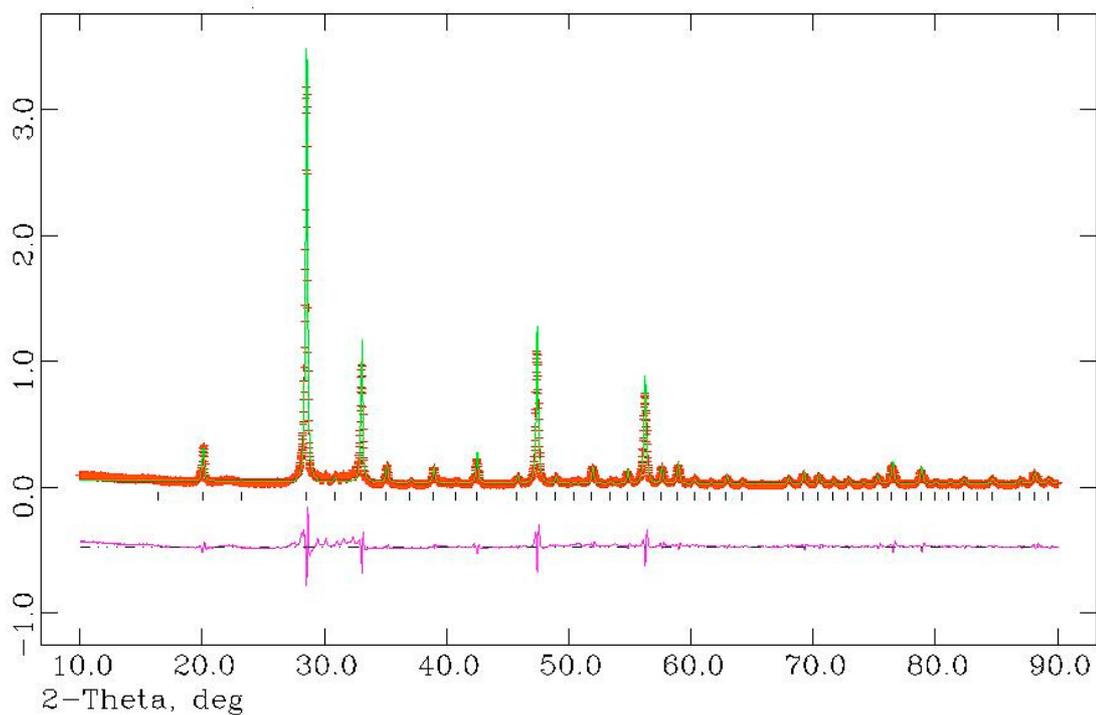
Figure 7.1 XRPD pattern for sample (1) Eu$_2$O$_3$. Intensity in arbitrary units.
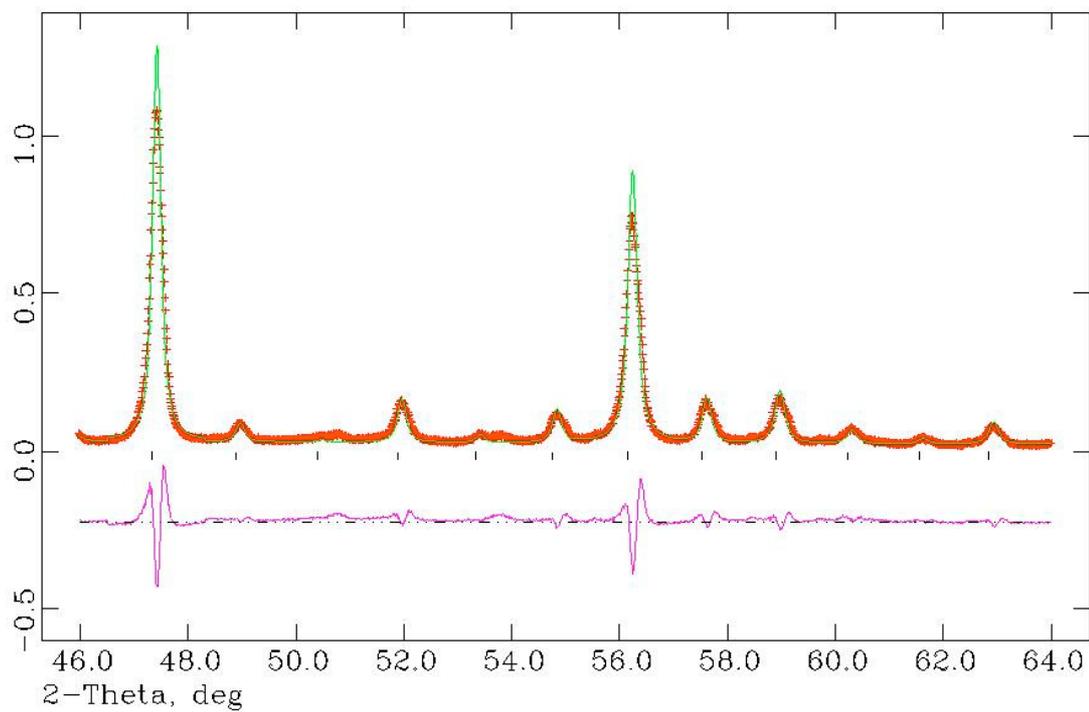
Figure 7.2 XRPD pattern for sample (1) Eu$_2$O$_3$ showing the region between 46° and 64° in more detail.

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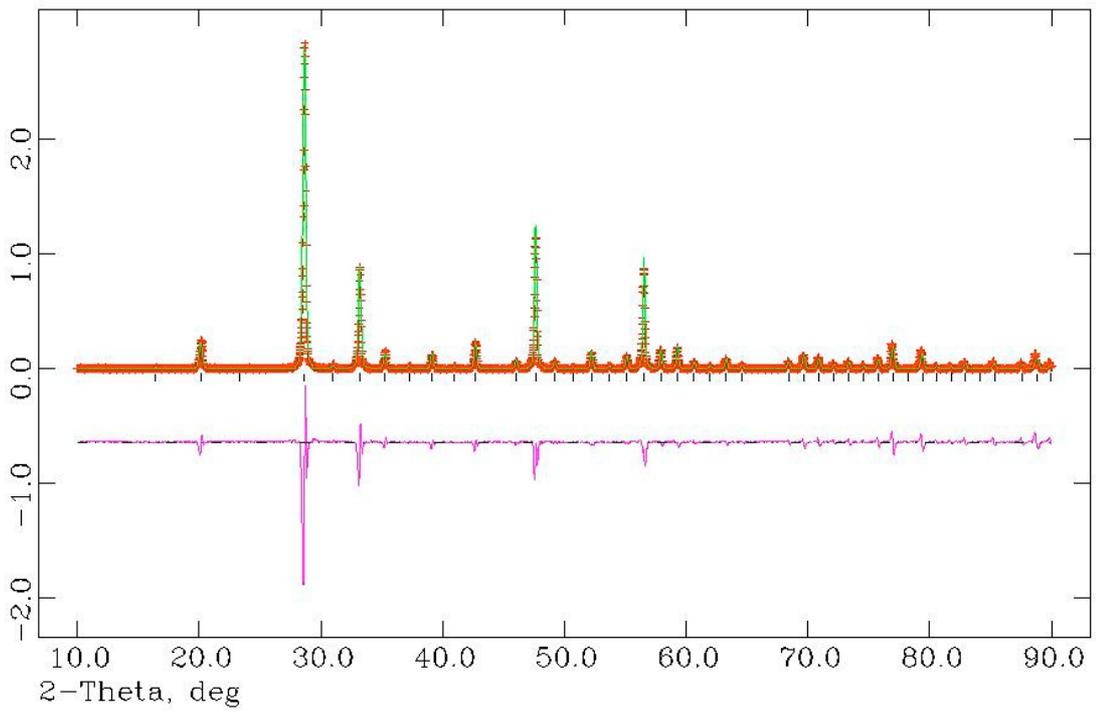
Figure 7.3 XRPD pattern for sample (2) Gd$_2$O$_3$.
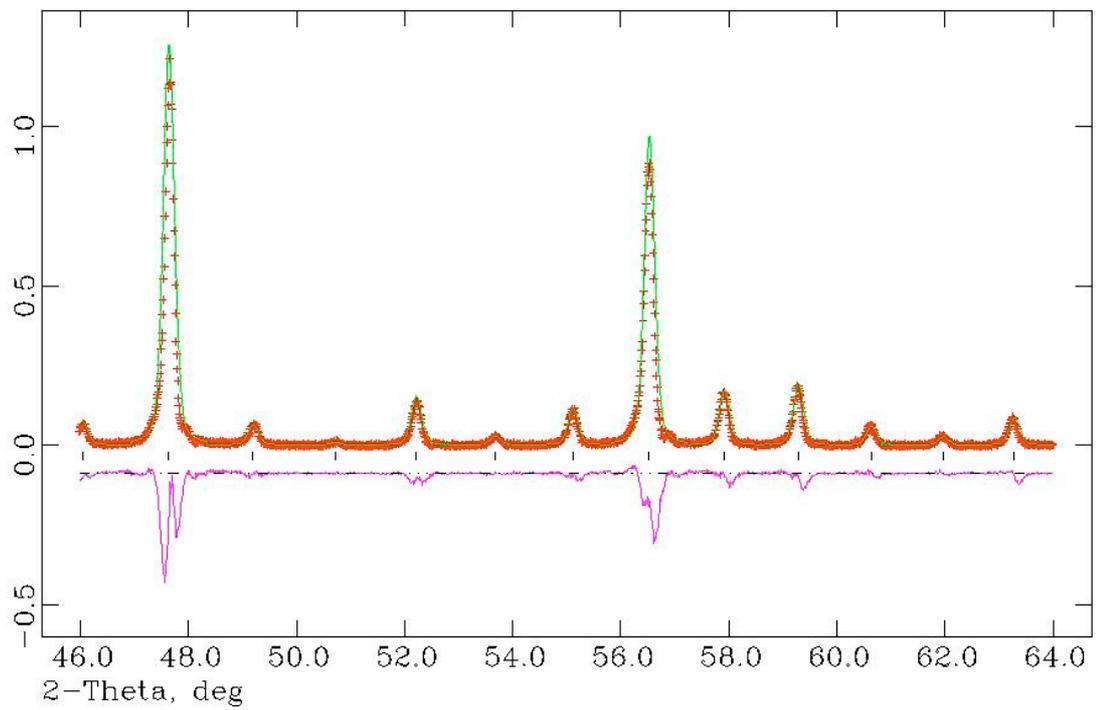
Figure 7.4 XRPD pattern for sample (2) Gd$_2$O$_3$ showing the region between 46° and 64° in more detail.
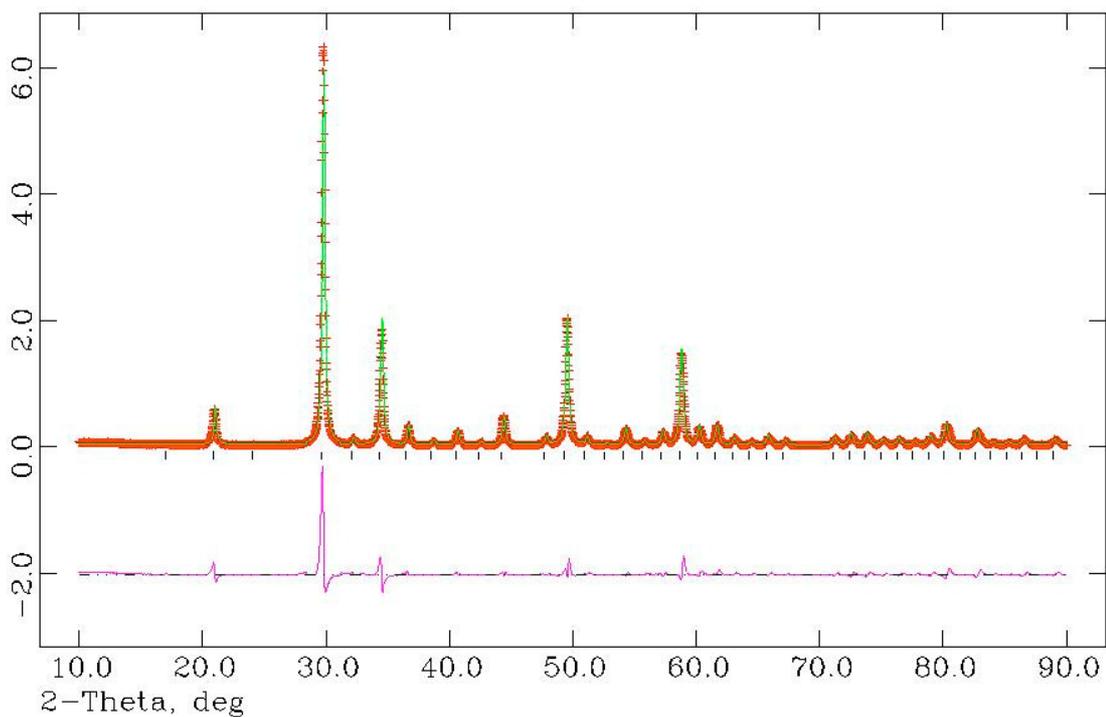
Figure 7.5 XRPD pattern for sample (3) Yb₂O₃.
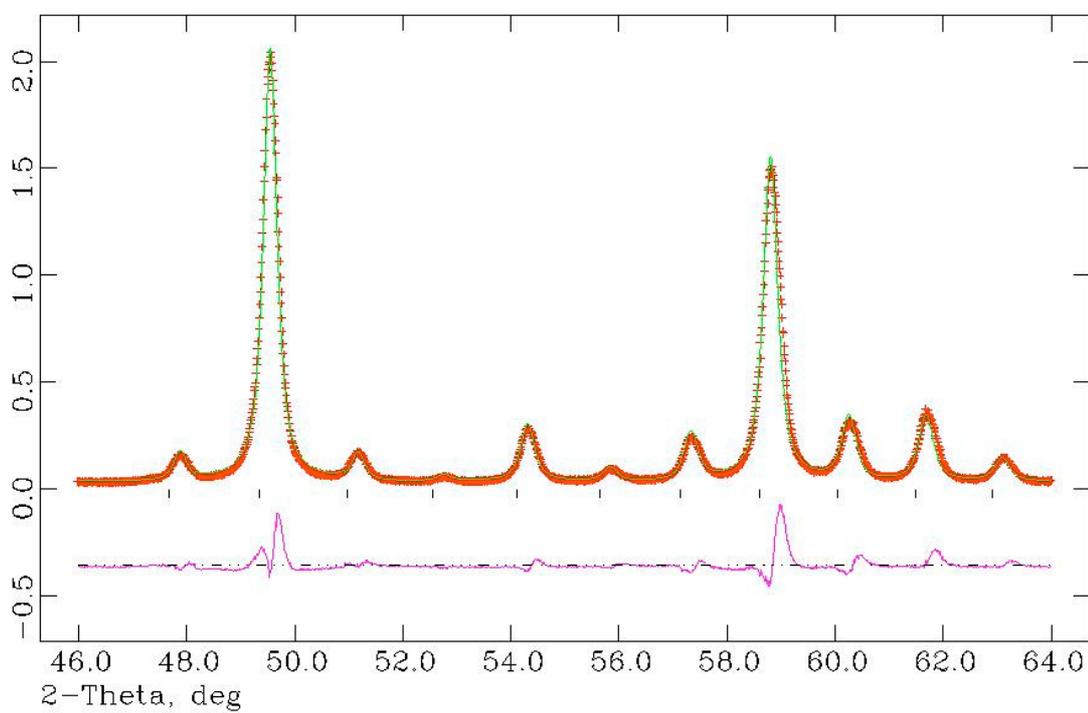
Figure 7.6 XRPD pattern for sample (3) Yb₂O₃ showing the region between 46° and 64° in more detail.
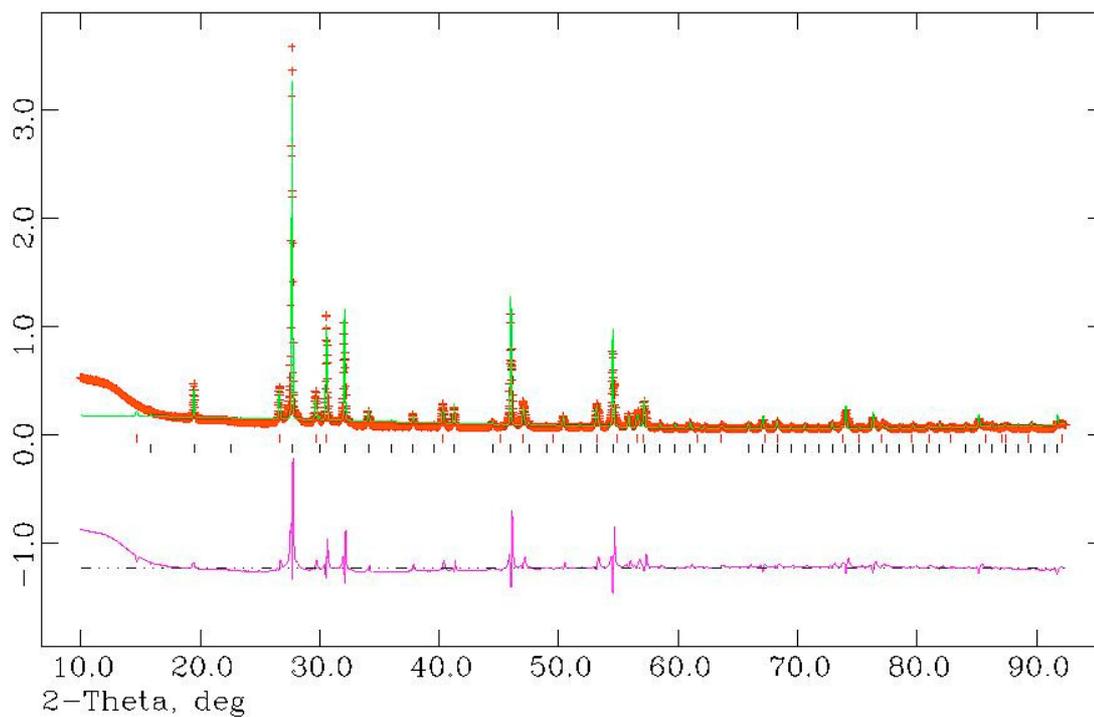
Figure 7.7 XRPD pattern for sample (4) Pr₂O₃. Upper tick marks show the hexagonal phase, lower tick marks cubic.
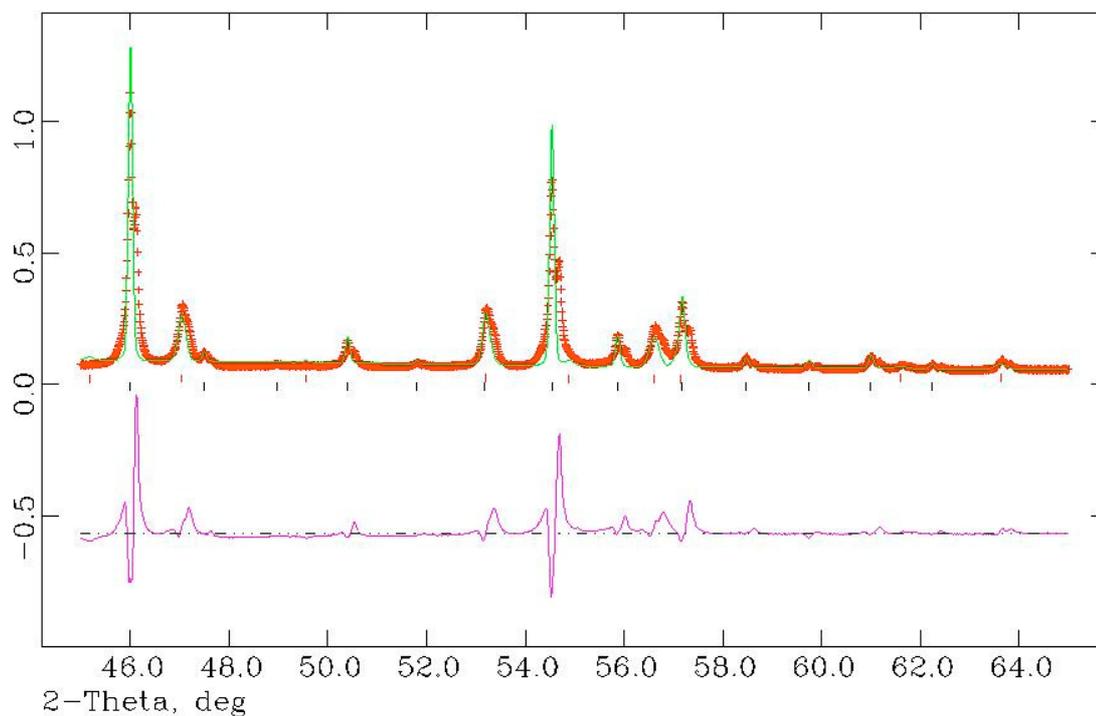
Figure 7.8 XRPD pattern for sample (4) Pr₂O₃ showing the region between 46° and 64° in more detail.
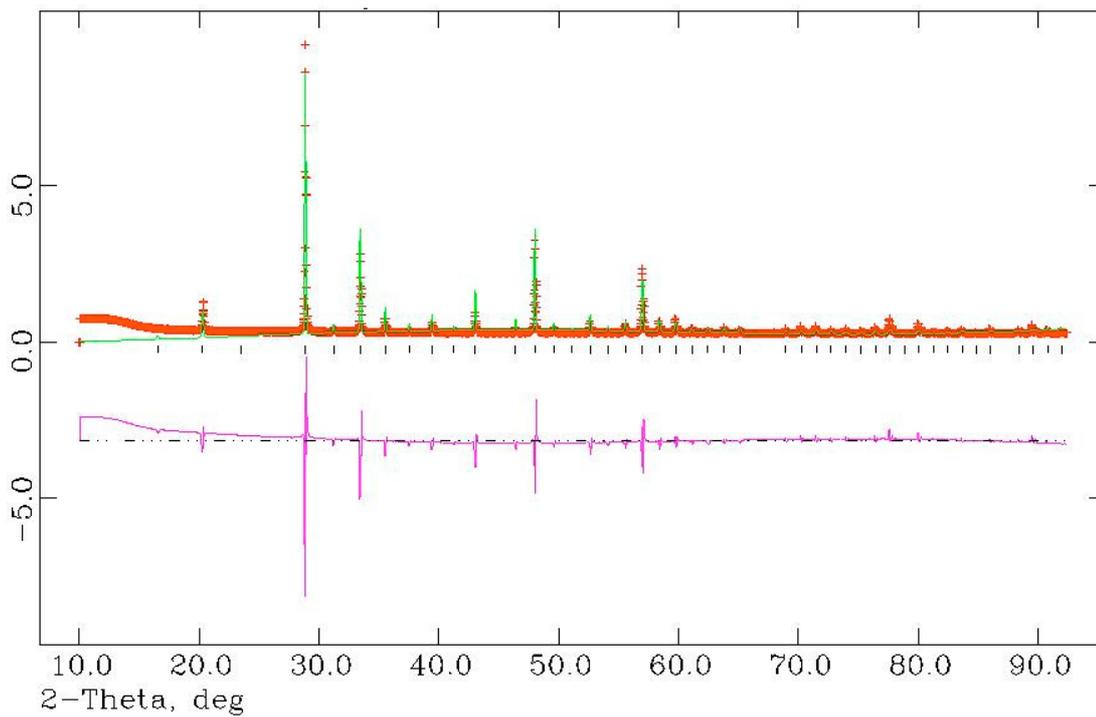
Figure 7.9 XRPD pattern for sample (5) Tb₂O₃
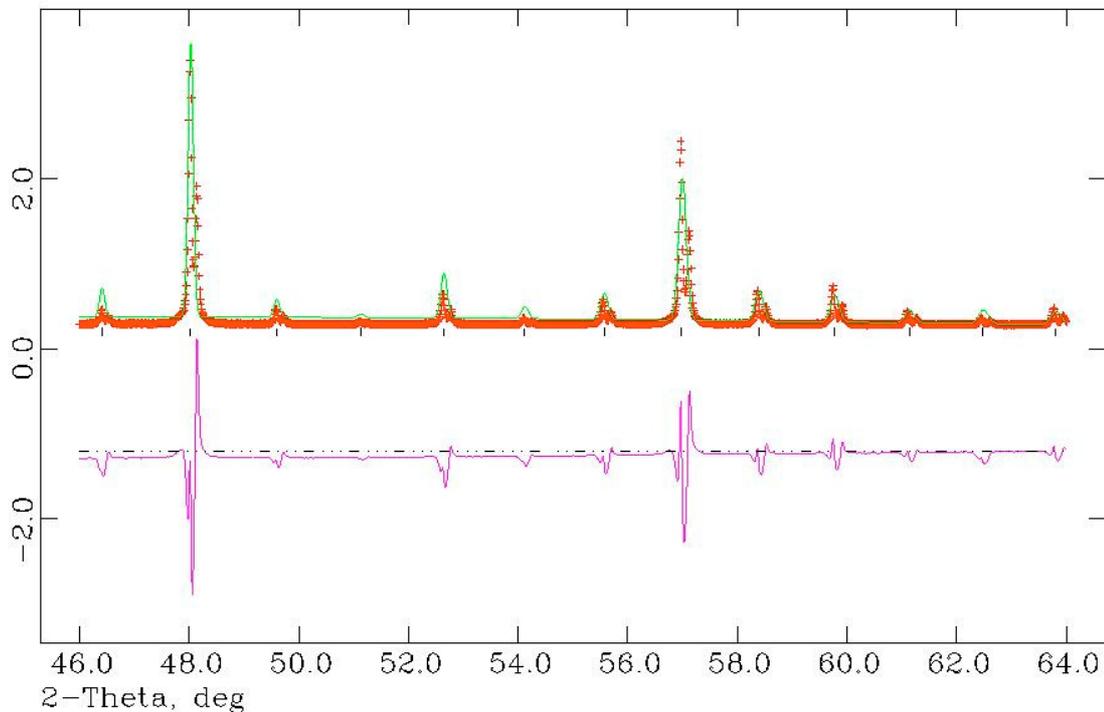
Figure 7.10 XRPD pattern for sample (5) Tb₂O₃ showing the region between 46° and 64° in more detail. Tick marks show reflections from both Cu Kα₁ and Kα₂ radiation.

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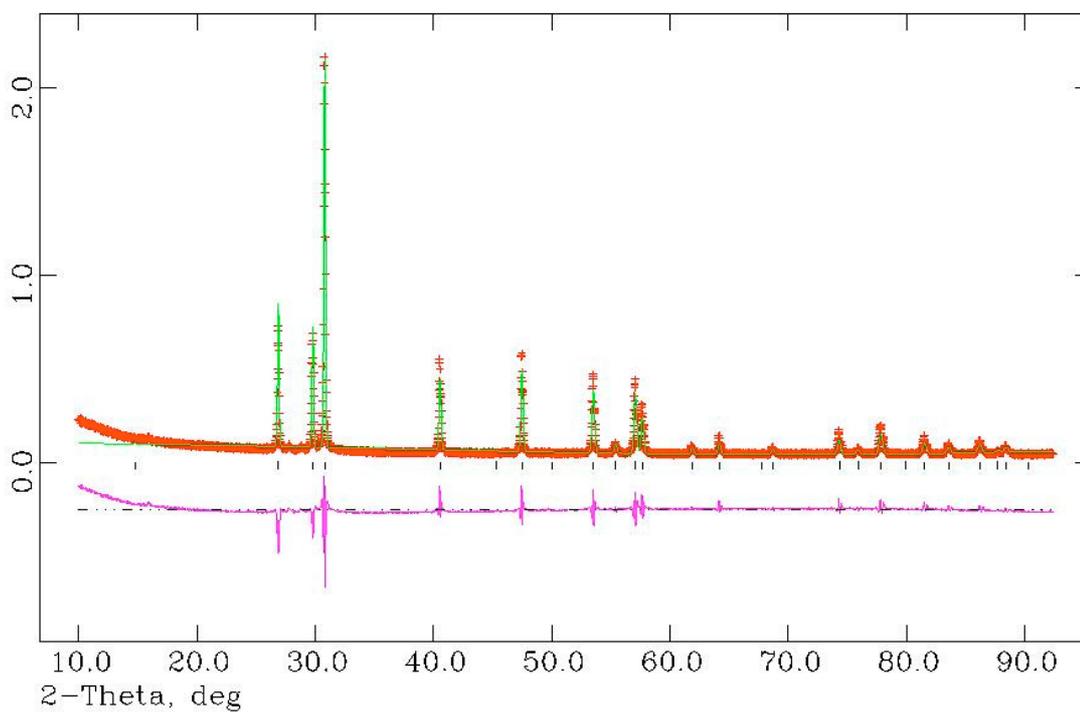
Figure 7.11 XRPD pattern for sample (9) Nd$_2$O$_3$.
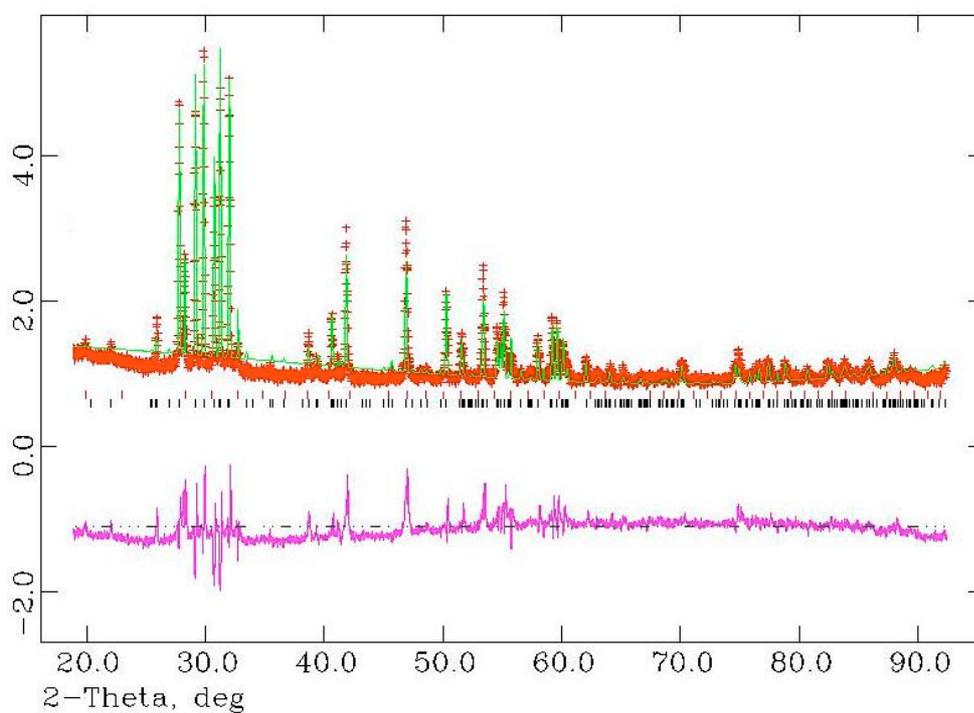
Figure 7.12 XRPD pattern for sample (10) Sm$_2$O$_3$. Upper tick marks show the cubic phase, lower tick marks monoclinic.
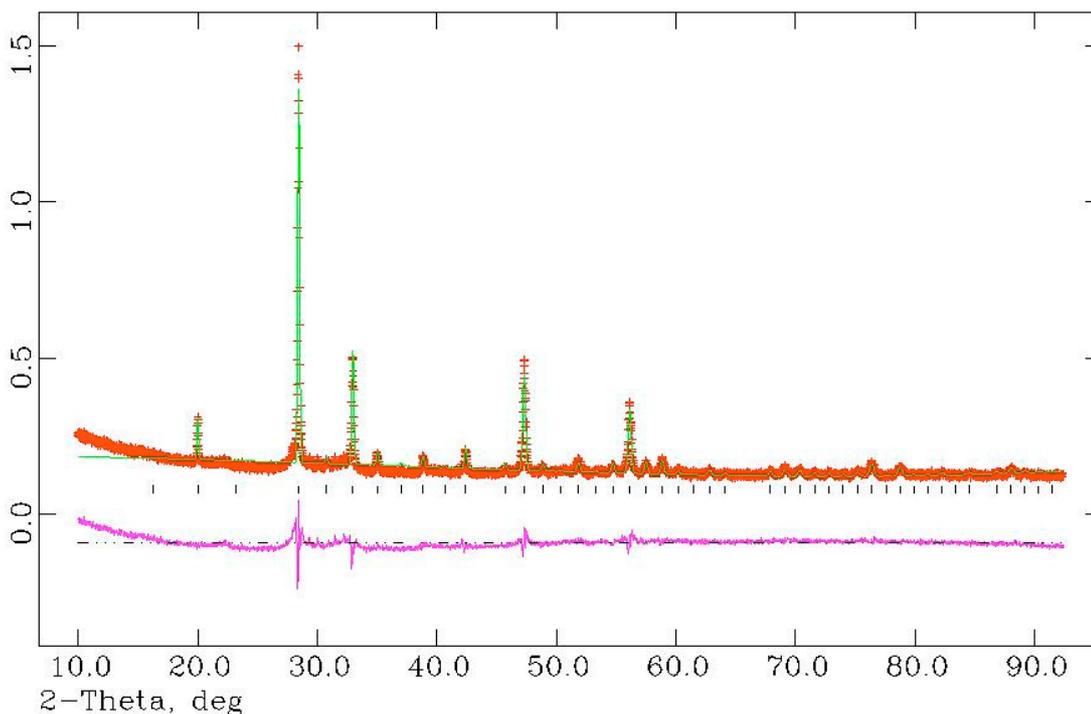
Figure 7.13 XRPD pattern for sample (11) Eu₂O₃.

7.1.2 Ambient temperature cell types

The unit cell parameters for sample (1) to (5) and (9) to (11) are given in table 7.1 below.

Sample	Material	Phase	Cell parameters (Å)	Space group
(1)	Eu_2O_3	Cubic	a = 10.860(2)	Ia-3
(2)	Gd_2O_3	Cubic	a = 10.786(2)	Ia-3
(3)	Pr_2O_3	Cubic 56%	a = 11.152(2)	Ia-3
		Hexagonal 44%	a = 3.860(2)	P-3m1
			c = 6.017(2)	
(4)	Yb_2O_3	Cubic	a = 10.437(2)	Ia-3
(5)	Tb_2O_3	Cubic	a = 10.711(2)	Ia-3
(9)	Nd_2O_3	Hexagonal	a = 3.828(2)	P-3m1
			c = 5.996(2)	
(10)	Sm_2O_3	Monoclinic 97%	a = 14.168(2),	$C2/m$
			b = 3.624(2),	
			c = 8.848(2),	
			β = 100.05°	
		Cubic 3%	a = 10.928(2)	Ia-3
(11)	Eu_2O_3	Cubic	a = 10.860(2)	Ia-3

Table 7.1 Refined unit cell parameters for samples (1) to (5) and (9) to (11).

To reflect the lanthanide contraction, the following image shows unit cell parameter against atomic number for the cubic cells in table 7.1.
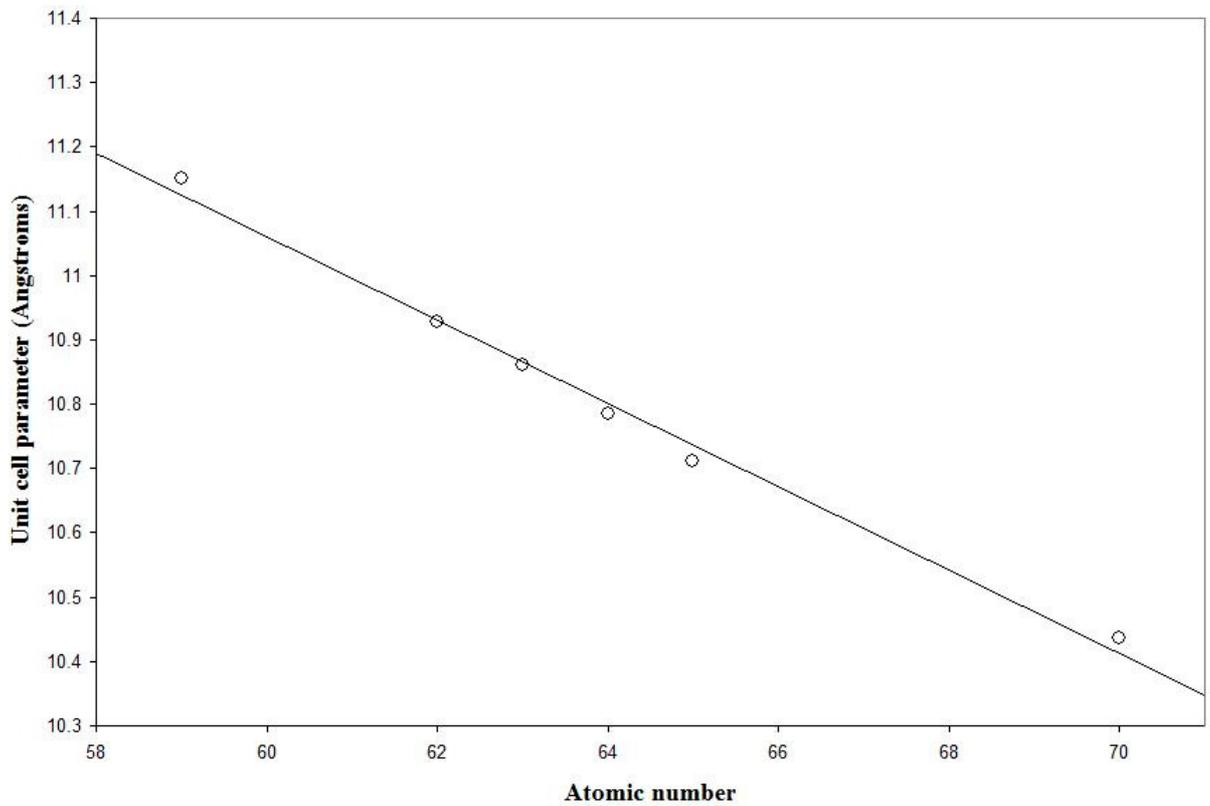
Figure 7.14 Plot of unit cell parameter against atomic number for the C-type cell. Error bars are within the data points.

Analysis of the data in figure 7.14 showed that the unit cell parameter decreased on average by 0.065Å for each unit increase in atomic number.

7.1.3 Ambient temperature crystal structures

The cell contents after refinement for all phases are given below.

7.1.3.1 The C-type phase
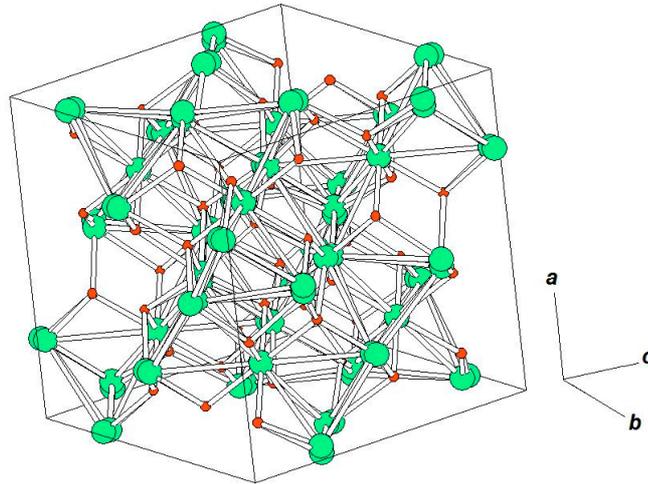
Figure 7.15 Crystal structure of the C-type cubic phase in space group Ia-3. Larger spheres represent the metallic atoms.

Pr_2O_3 $a = 11.152(2)$Å, sg *Ia*-3, $R_{wp} = 0.3271*$

Site	x	y	Z	Occupancy
Pr1	0.25	0.25	0.25	1
Pr2	0.973872	0	0.25	1
O1	0.364587	0.151367	0.364111	1

*Table 7.2 Crystal structure of cubic Pr_2O_3. *total value for the C and A mixed phase.*

Eu_2O_3 sample (1) $a = 10.860(2)$Å, sg *Ia*-3, $R_{wp} = 0.2151$

Site	x	y	z	Occupancy
Eu1	0.25	0.25	0.25	1
Eu2	0.96958	0	0.25	1
O1	0.39050	0.15783	0.38611	1

Table 7.3 Crystal structure of cubic Eu_2O_3.

Eu$_2$O$_3$ sample (11) $a = 10.860(2)$Å, sg *Ia*-3, R$_{wp}$ = 0.0741

Site	x	y	z	Occupancy
Eu1	0.25	0.25	0.25	1
Eu2	0.969358	0	0.25	1
O1	0.396584	0.147428	0.399414	1

Table 7.4 Crystal structure of cubic Eu$_2$O$_3$.

Gd$_2$O$_3$ $a = 10.786(2)$Å, sg Ia-3, R$_{wp}$ = 0.5869

Site	x	Y	z	Occupancy
Gd1	0.25	0.25	0.25	1
Gd2	0.969583	0	0.25	1
O1	0.39107	0.15586	0.37911	1

Table 7.5 Crystal structure of cubic Gd$_2$O$_3$.

Tb$_2$O$_3$ $a = 10.711(2)$Å, sg *Ia*-3

Site	x	y	z	Occupancy
Tb1	0.25	0.25	0.25	1
Tb2	0.958688	0	0.25	1
O1	0.373145	0.156786	0.350571	1

Table 7.6 Crystal structure of cubic Tb$_2$O$_3$.

Yb$_2$O$_3$ $a = 10.437(2)$Å, sg *Ia*-3(206), R$_{wp}$ = 0.2164

Atom	X	y	z	Occupancy
Yb1	0.25	0.25	0.25	1
Yb2	0.96744	0	0.25	1
O1	0.39349	0.15304	0.38678	1

Table 7.7 Crystal structure of cubic Yb$_2$O$_3$.

7.1.3.2 The B-type phase
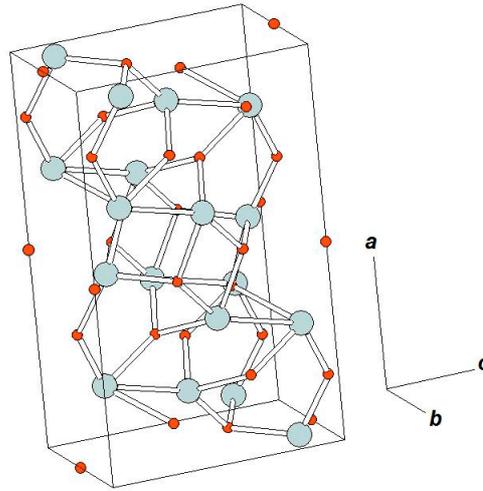
Figure 7.16 Crystal structure of the B-type monoclinc phase in space group C2/m. Larger spheres represent the metallic atoms.

Sm_2O_3 a = 14.168(2)Å, b = 3.624(2)Å, c = 8.848(2)Å, β = 100.05°, sg $C2/m$, R_{wp} = 0.1700

Site	x	y	z	Occupancy
Sm1	0.132074	0.5	0.500535	1
Sm2	0.193545	0.5	0.162728	1
Sm3	0.472639	0.5	0.201875	1
O1	0.101440	0	0.409000	1
O2	0.423910	0.5	0.047833	1
O3	0.399147	0.5	0.377914	1
O4	0.537647	0	0.445264	1
O5	0	0.5	0	1

Table 7.8 Crystal structure of monoclinic Sm_2O_3.

7.1.3.3 The A-type phase
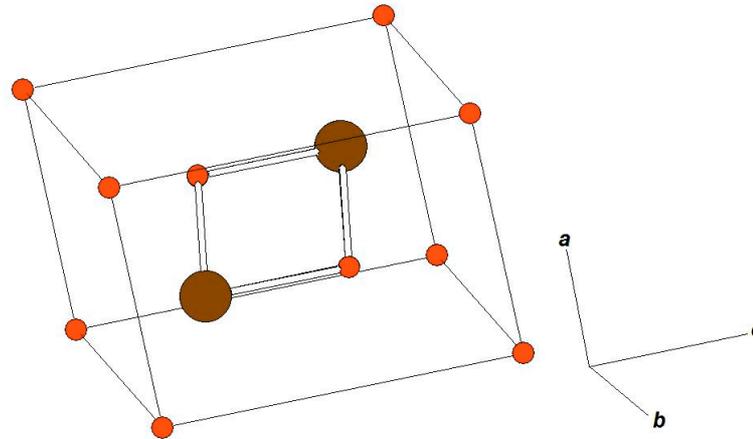
Figure 7.17 Crystal structure of the A-type hexagonal phase in space group P-3m1.
Larger spheres represent the metallic atoms.

Pr_2O_3 a = 3.860(2)Å, c = 6.017(2)Å, sg $P–3m1$, R_{wp} = 0.3271*

Site	x	y	z	Occupancy
Pr1	0.674413	0.325587	0.269493	1
Pr2	0.719677	0.280324	0.610808	1
O1	0	0	0	1

*Table 7.9 Crystal structure of hexagonal Pr_2O_3. *total value for the C and A mixed*

phase.

Nd_2O_3 a = 3.828(2)Å, c = 5.996(2)Å, sg $P–3m1$, R_{wp} = 0.2143

Site	x	y	z	Occupancy
Nd1	0.341433	0.658566	0.238656	1
Nd2	0.428594	0.714297	0.642839	1
O1	0	0	0	1

Table 7.10 Crystal structure of hexagonal Nd_2O_3.

7.1.4 Discussion on ambient temperature results

To obtain the above results, the diffraction patterns obtained were run through the
CRYSFIRE indexing suite, the indexing program GRAPHPRO and Chekcell to find
the best match and space group. Full profile Rietveld refinement was performed using
GSAS. The Gd_2O_3 pattern was successfully indexed using CRYSFIRE. However, the
patterns for Eu_2O_3, Pr_2O_3, Yb_2O_3, Tb_2O_3, Nd_2O_3 and Sm_2O_3 could not be indexed using

CRYSFIRE. GRAPHPRO was used to determine the unit cell parameters for sample (1) Eu_2O_3, Yb_2O_3, Tb_2O_3 and sample (11) Eu_2O_3, the initial values being $a = 10.828$Å, 10.405Å, 10.699Å and 10.8232Å respectively. Relaxing the 2θ tolerance in CRYSFIRE from the default of 0.04 degrees to 0.1 degrees meant that CRYSFIRE was able to locate solutions for Eu_2O_3 (10.8379Å), Yb_2O_3 (10.4068Å) and Nd_2O_3 ($a = 3.828$Å, $c = 5.994$Å). Relaxing the tolerance further to 0.15 degrees meant the indexing of Tb_2O_3 was successful (10.712Å). The space group in each case was found to be Ia-3 via Chekcell. GRAPHPRO was unable to index the Pr_2O_3 pattern.

As might be expected, the patterns for the cubic cells appear essentially the same for all samples, with just slight shifts on the 2θ axis reflecting the changes in unit cell parameter. With increasing atomic number of the rare earth metal, the unit cell parameter decreases according to the lanthanide contraction (shown in figure 7.14) and 2θ positions increase according to the Bragg equation. However, for Eu_2O_3 there were a number of low-intensity lines around $2\theta = 30°$ which could not be explained by the cubic indexing. Since the phase diagram implied that no high-temperature phase existed at ambient temperature, these were at first thought to be due to an impurity. However, it will be shown later that this was due to the unexpected presence of the high-temperature modification.

The pattern for sample (3) Pr_2O_3 was different to those of the other samples because it contained many more peaks. Analysis of the data showed that the sample consisted of both cubic and hexagonal phases, which is consistent with the phase diagram in chapter 1. Its cubic cell was estimated at 11.2Å by extrapolation from the other known cubic cells in the series. Taking the initial atom positions to be the same as for europia, GSAS was used to refine the cubic cell to a parameter of 11.152Å. Once the cubic lines in the pattern were identified, CRYSFIRE was run on the remaining lines to index the other cell contributing to the pattern. GSAS was again used to refine this cell to $a = 3.860$Å and $c = 6.017$Å. Analysis of the pattern from the refined phase fractions in GSAS showed there to be approximately 56% of the cubic phase and 44% of the hexagonal phase present.

From figure 1.5 Nd_2O_3 was provisionally expected to be cubic with a cell side around 11.06Å (found by interpolation), or perhaps mixed phase. However, the histogram showed there to be 100% hexagonal (high-temperature) phase present.

Again from figure 1.5, Sm_2O_3 was expected to show cubic phase (10.93Å by interpolation) with perhaps a small degree of monoclinic. However, the histogram showed there to be 97% monoclinic phase present. The supplier was contacted and stated that the crystal structure should be cubic. However, on further enquiry it was found that the sesquioxide had been generated via a multi-stage process, by dissolving the bastnaesite ore in acid, precipitating the carbonate and calcining to the oxide. As the material had been exposed to elevated temperature in its preparation, the monoclinic phase was already present in the commercial sample.

7.2 XRPD AFTER ANNEALING

7.2.1 Diffraction patterns

The XRPD patterns recorded after annealing are shown in figures 7.18 to 7.27 below. Rietveld refinements of the data were carried out where significant conversion to the high temperature phase had occurred (figures 7.18, 7.21, 7.22, 7.26, 7.27).
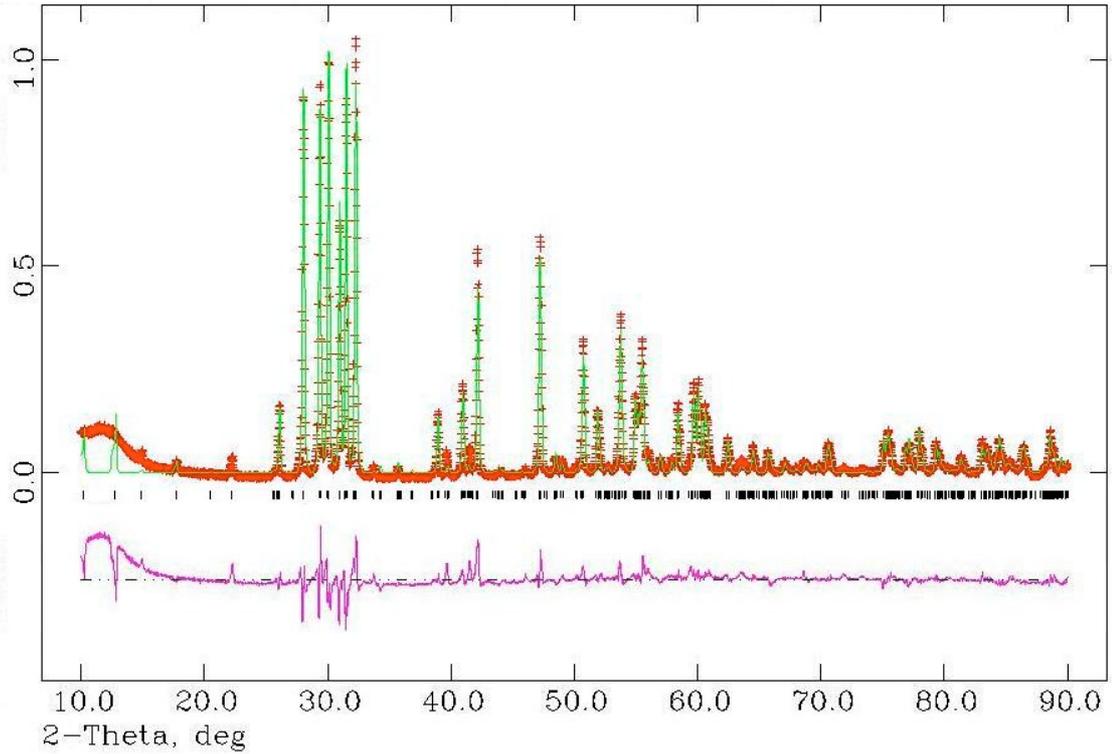
Figure 7.18 XRPD pattern for sample (1) Eu_2O_3 following 1 hour anneal at 1334ºC and slow cooling.
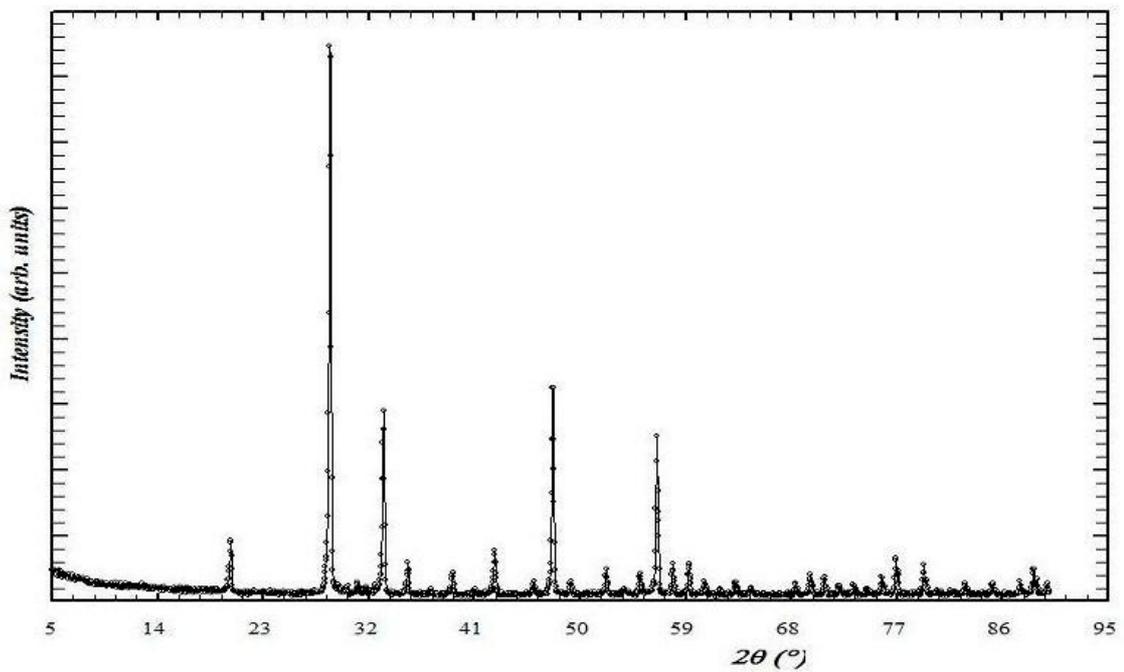
Figure 7.19 XRPD pattern for sample (2) Gd_2O_3 following 1 hour anneal at 1334ºC and slow cooling.
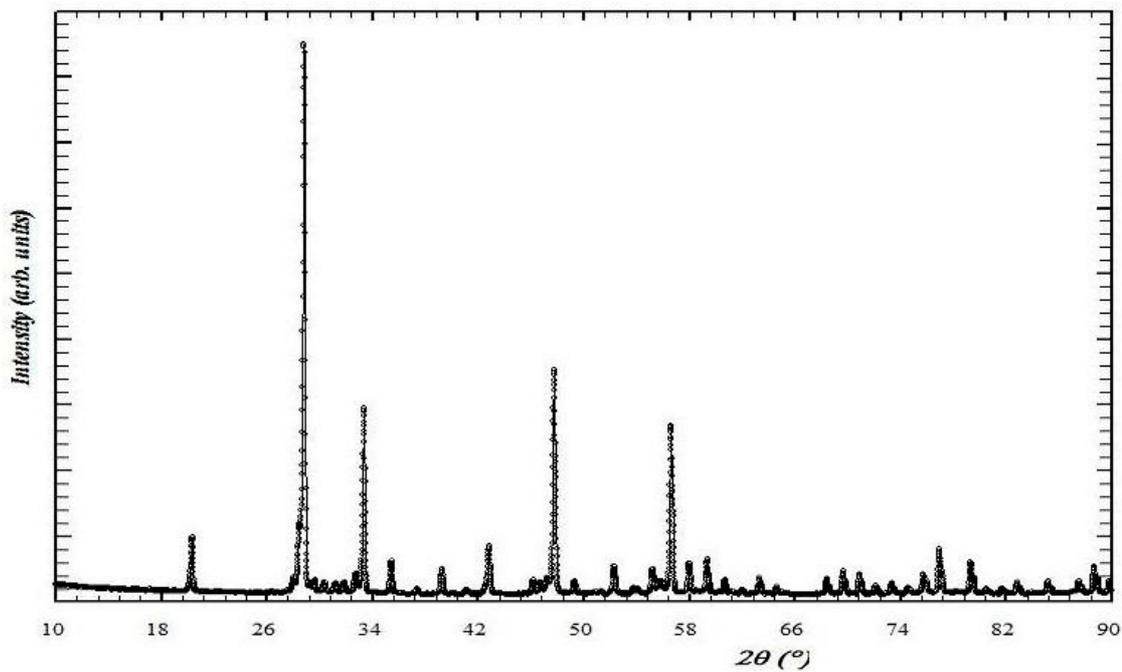
Figure 7.20 XRPD pattern for sample (2) Gd$_2$O$_3$ following 1 hour anneal at 1500ºC and quenching.
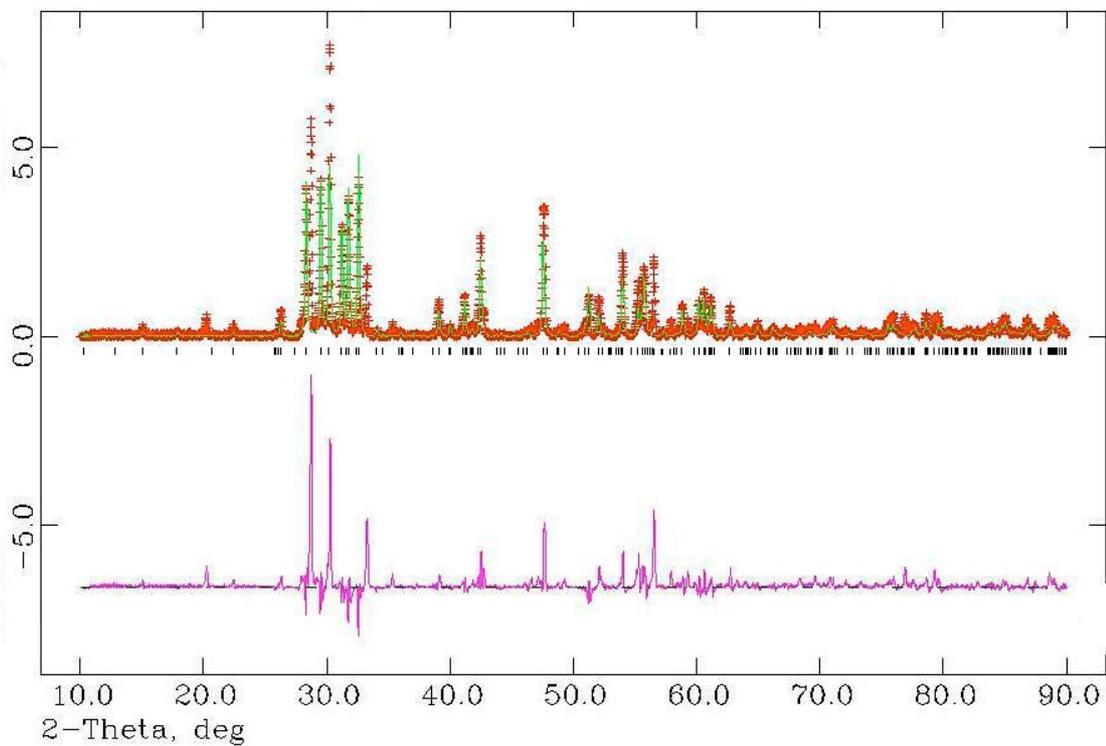
Figure 7.21 XRPD pattern for sample (2) Gd$_2$O$_3$ following 7 hour anneal at 1500ºC and quenching.
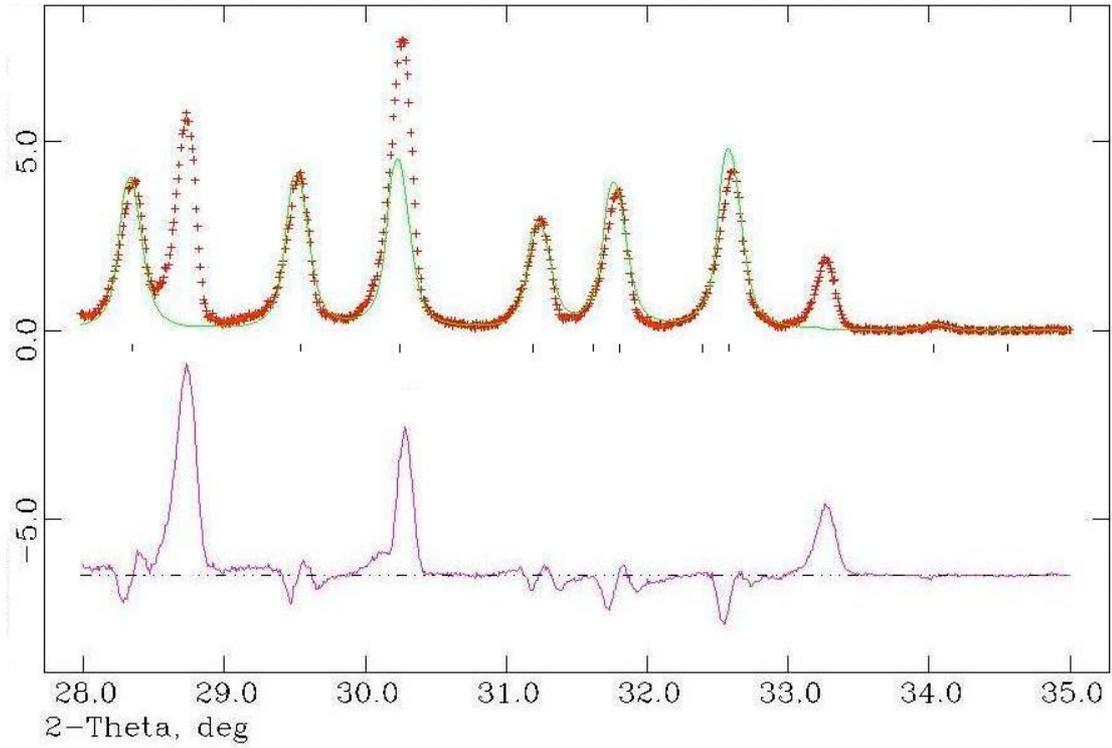
Figure 7.22 XRPD pattern for sample (2) Gd_2O_3 following 7 hour anneal at 1500ºC and quenching showing the region between 28° and 35° in more detail.
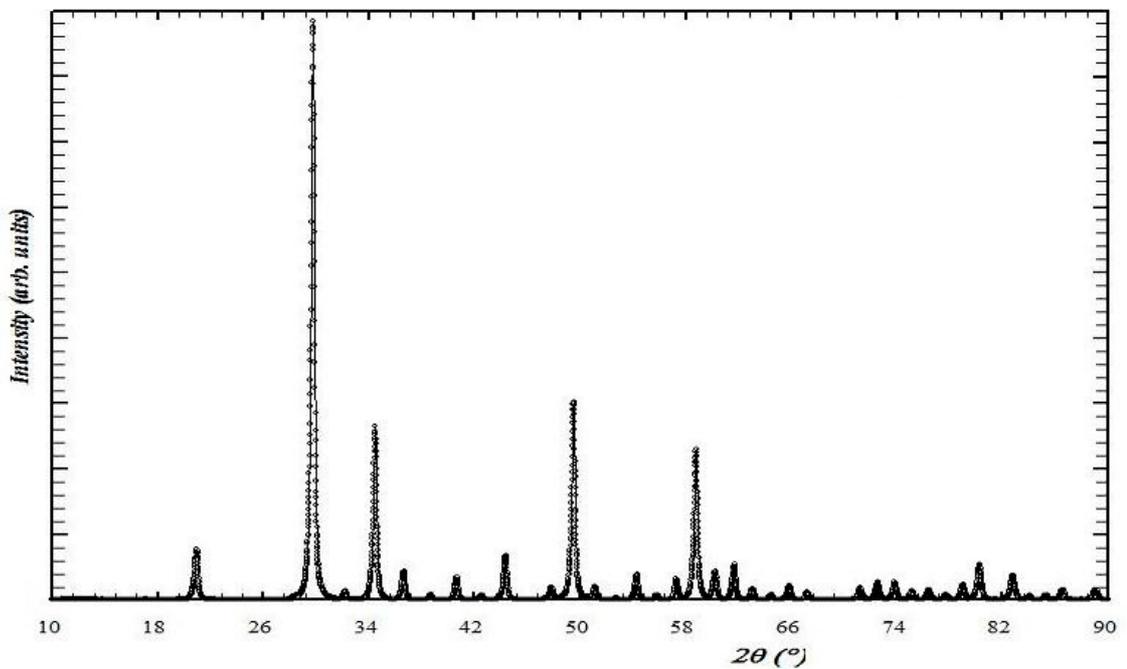
Figure 7.23 XRPD pattern for sample (3) Yb_2O_3 following 1 hour anneal at 1500ºC and quenching.
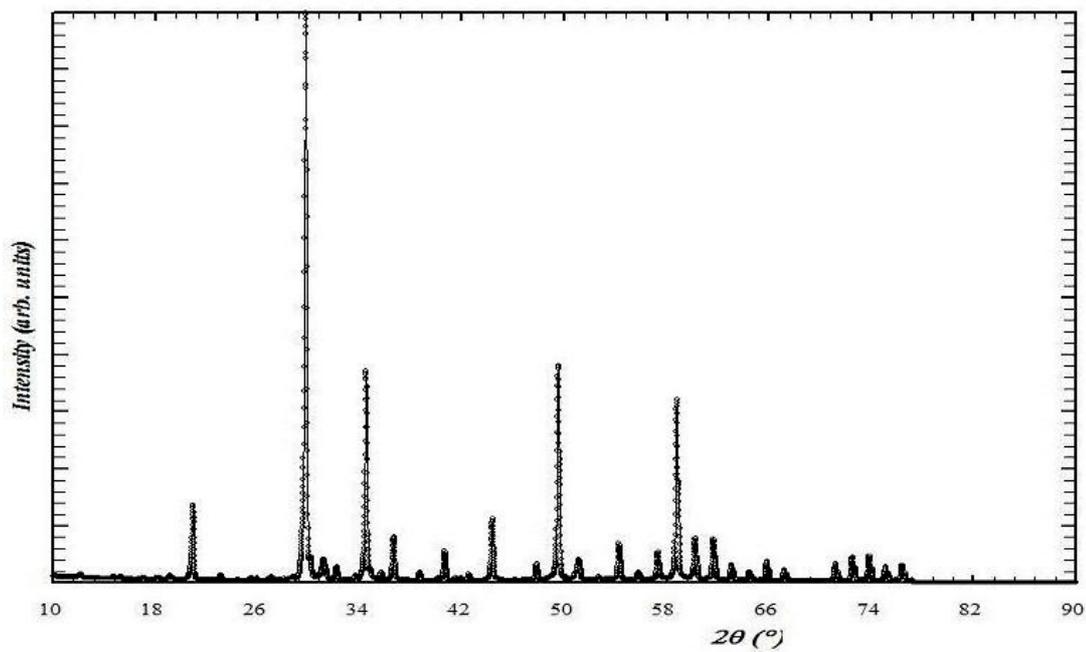
Figure 7.24 XRPD pattern for sample (3) Yb$_2$O$_3$ following 5 hour anneal at 1500ºC and quenching.
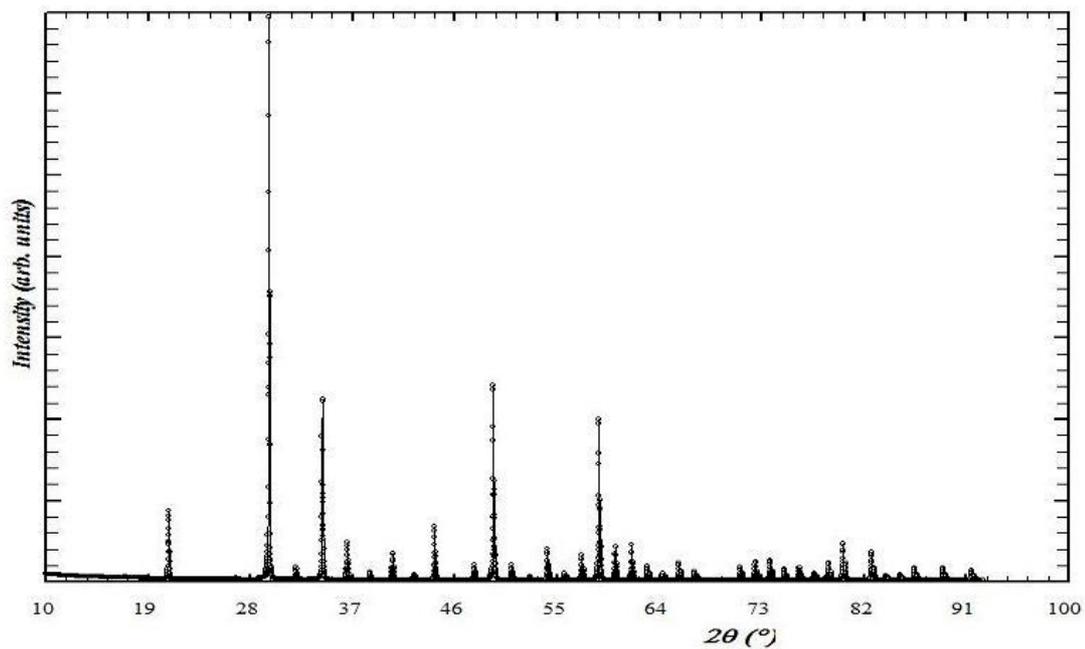
Figure 7.25 XRPD pattern for sample (7) Yb$_2$O$_3$ following 5 hour anneal at 1800ºC and quenching.
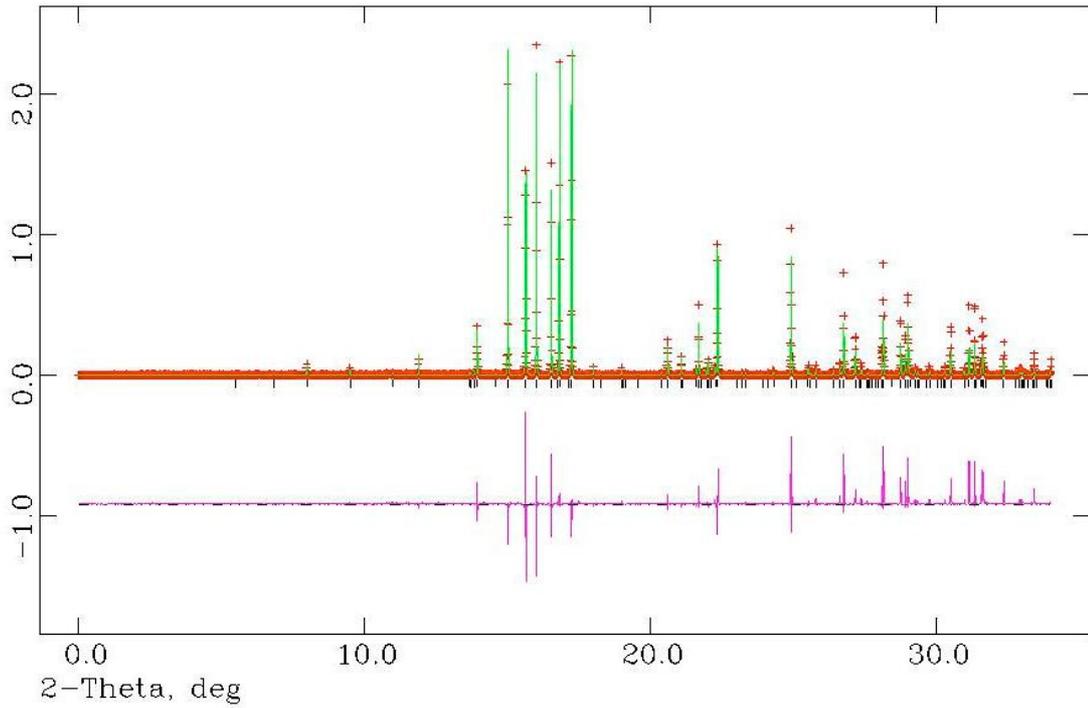
Figure 7.26 XRPD pattern for sample (8) Gd$_2$O$_3$ following 7 hour anneal at 1500ºC and quenching.
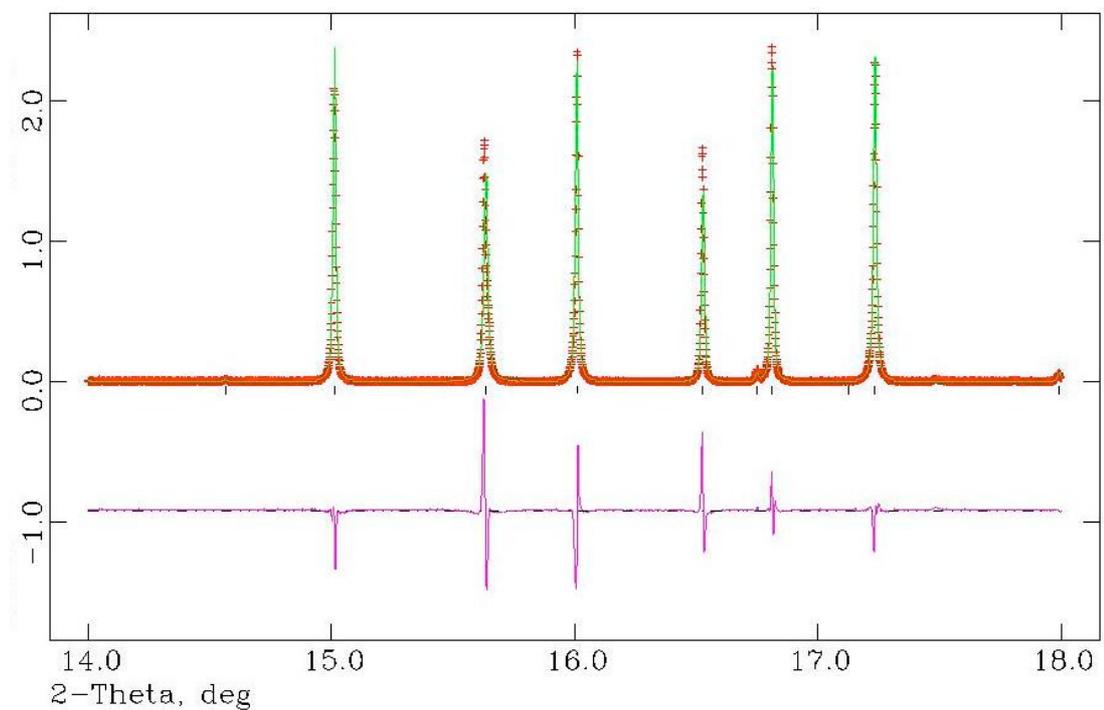
Figure 7.27 XRPD pattern for sample (8) Gd$_2$O$_3$ following 7 hour anneal at 1500ºC and quenching showing the region between 14° and 18° in more detail.

7.2.2 Cell types following annealing

The unit cell parameters for samples (1), (2), (3), (7) and (8) following annealing are given in table 7.11 below.

Sample	Anneal	Phase	Cell parameters (Å)	Space group
(1) Eu_2O_3	1 hour at 1334°C	Monoclinic 95% (Cubic 5%)	$a = 14.110(2)$ $b = 3.602(2)$ $c = 8.808(2)$ $\beta = 100.06°$	C2/m
(2) Gd_2O_3	1 hour at 1334°C	Cubic 99% (Monoclinic 1%)	$a = 10.860(2)$	Ia-3
(2) Gd_2O_3	1 hour at 1500°C	Cubic 99% (Monoclinic 1%)	$a = 10.860(2)$	Ia-3
(2) Gd_2O_3	7 hours at 1500°C	Monoclinic 97% (Cubic 3%)	$a = 14.073(2)$ $b = 3.572(2)$ $c = 8.755(2)$ $\beta = 100.03°$	C2/m
(3) Yb_2O_3	1 hour at 1500°C	Cubic 99% (Monoclinic 1%)	$a = 10.406(2)$	Ia-3
(3) Yb_2O_3	5 hours at 1500°C	Cubic 99% Monoclinic 1%	$a = 10.406(2)$ $a = 13.740(2)$ $b = 3.400(2)$ $c = 8.593(2)$ $\beta = 100.12°.$	Ia-3 C2/m
(7) Yb_2O_3	5 hours at 1800°C	Cubic 100%	$a = 10.435(2)$	Ia-3
(8) Gd_2O_3	7 hours at 1500°C	Monoclinic 100%	$a = 14.0980(8)$ $b = 3.5750(8)$ $c = 8.7670(8)$ $\beta = 100.08°$	C2/m

Table 7.11 Unit cell parameters for samples (1), (2), (3), (7) and (8) after annealing..

To reflect the lanthanide contraction, the following image shows unit cell parameters against atomic number for the monoclinic cells in tables 7.1 and 7.11.

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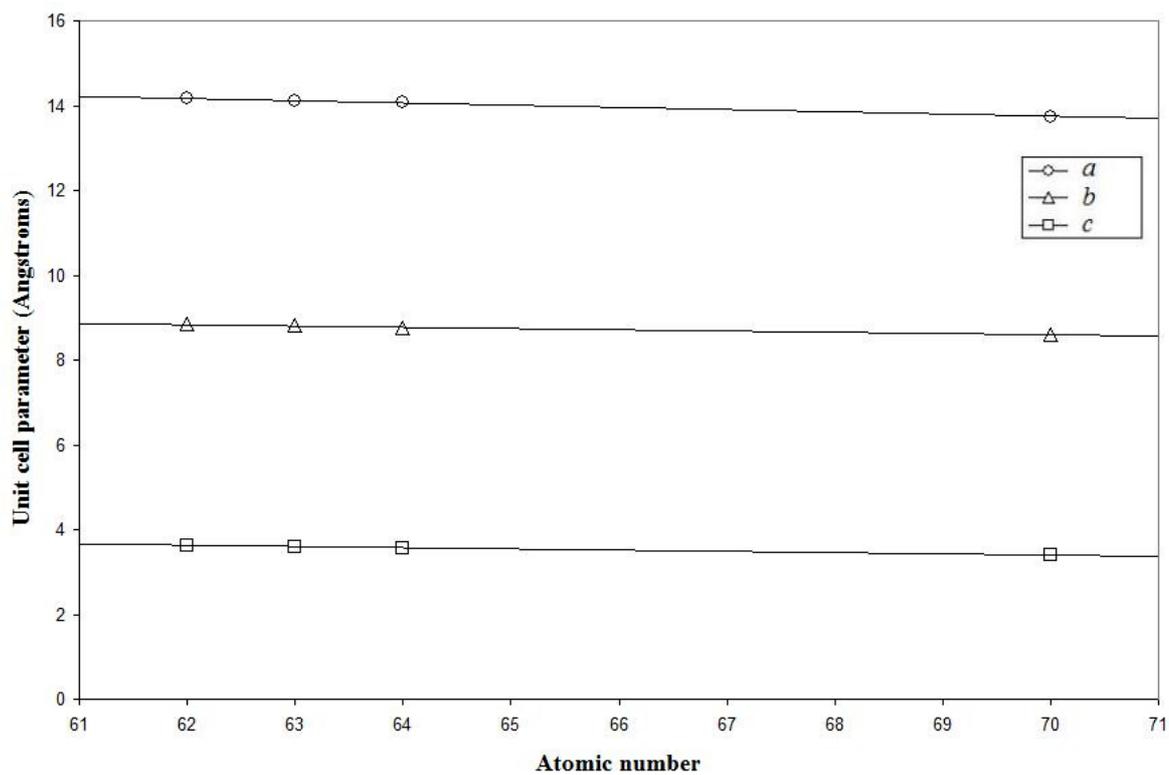
Figure 7.28 Plot of unit cell parameter against atomic number for the B-type cell.
Error bars are within the data points.

7.2.3 High-temperature crystal structures

The cell contents for all phases after refinement are given below. For completeness, the structures for gadolinia taken from both laboratory and synchrotron data are included.

7.2.3.1 The B-type phase

Eu$_2$O$_3$ a = 14.110(2)Å, b = 3.602(2)Å, c = 8.808(2)Å, β = 100.06°, sg *C2/m*

Site	x	y	z	Occupancy
Eu1	0.13325	0.5	0.49001	1
Eu2	0.19061	0.5	0.14136	1
Eu3	0.46897	0.5	0.19012	1
O1	0.11556	0	0.28831	1
O2	0.36952	0.5	0.00401	1
O3	0.38693	0.5	0.40872	1
O4	0.48730	0	0.36007	1
O5	0	0.5	0	1

Table 7.12 Crystal structure of monoclinic Eu$_2$O$_3$.

Gd$_2$O$_3$ a = 14.073(2)Å, b = 3.572(2)Å, c = 8.755(2)Å, β = 100.03°, sg *C2/m*, R$_{wp}$ =

0.5147

Site	x	y	Z	Occupancy
Gd1	0.13229	0.5	0.48514	1
Gd2	0.19332	0.5	0.13665	1
Gd3	0.47041	0.5	0.18702	1
O1	0.12246	0	0.32855	1
O2	0.34297	0.5	0.00172	1
O3	0.30732	0.5	0.36905	1
O4	0.48348	0	0.33026	1
O5	0	0.5	0	1

Table 7.13 Crystal structure of monoclinic Gd$_2$O$_3$ from lab data.

Gd$_2$O$_3$ a = 14.0980(2)Å, b = 3.5750(2)Å, c = 8.7670(2)Å, β = 100.08°, sg *C2/m*, R$_{wp}$ =

0.4709

Site	x	y	z	Occupancy
Gd1	0.13485	0.5	0.48879	1
Gd2	0.18928	0.5	0.13617	1
Gd3	0.46561	0.5	0.18799	1
O1	0.12638	0	0.28385	1
O2	0.33025	0.5	0.04017	1
O3	0.29291	0.5	0.37098	1
O4	0.47671	0	0.35531	1
O5	0	0.5	0	1

Table 7.14 Crystal structure of monoclinic Gd$_2$O$_3$ from synchrotron data.

7.2.3.2 Praseodymia β phase (Pr₆O₁₁)

$$a = 5.4790(2)\text{Å, sg } Fm\text{-}3m$$

Site	x	y	z	Occupancy
Pr1	0	0	0	1
O1	0.25	0.25	0.25	0.915

Table 7.15 Crystal structure of Pr₆O₁₁.

7.2.3.3 Praseodymia ι phase (Pr₇O₁₂)

$$a = 10.3460(2)\text{Å, } c = 9.6430(2) \text{ Å, space group } R\text{-}3, R_{wp} = 0.2957$$

Atom	x	y	z	Occupancy
Pr1	0	0	0	1
Pr2	0.121139	0.411048	0.006016	1
O1	0.166206	0.280304	0.447745	1
O2	0.249534	0.104719	0.083884	1

Table 7.16 Crystal structure of Pr₇O₁₂.

7.2.4 Discussion on annealed sample results

7.2.4.1 Europia

Indexing of the (1) Eu_2O_3 pattern taken post-heating using CRYSFIRE/Chekcell gave a monoclinic cell with $a = 14.110$Å, $b = 3.602$Å, $c = 8.808$Å, $\beta = 100.06°$ and space group $C2/m$. The cubic pattern was found to have almost completely disappeared. Interestingly, the inexplicable lines present in the diffraction pattern from the cubic phase had intensified, indicating that the feature initially thought to be caused by impurity was due to the presence of a small proportion of monoclinic phase in the commercially-obtained material. Further analysis of the ambient temperature pattern in figure 7.1 using GSAS showed there to be approximately 95% of the monoclinic phase and 5% of the cubic phase present.

7.2.4.2 Gadolinia

The pattern for (2) Gd_2O_3 obtained after 1 hour in the Carbolite furnace at 1334ºC appeared virtually identical to that prior to annealing. However, there was a small but noticeable change in the appearance of a number of extremely low-intensity reflections around the $2\theta = 30°$ mark, as shown in figure 7.29 below.
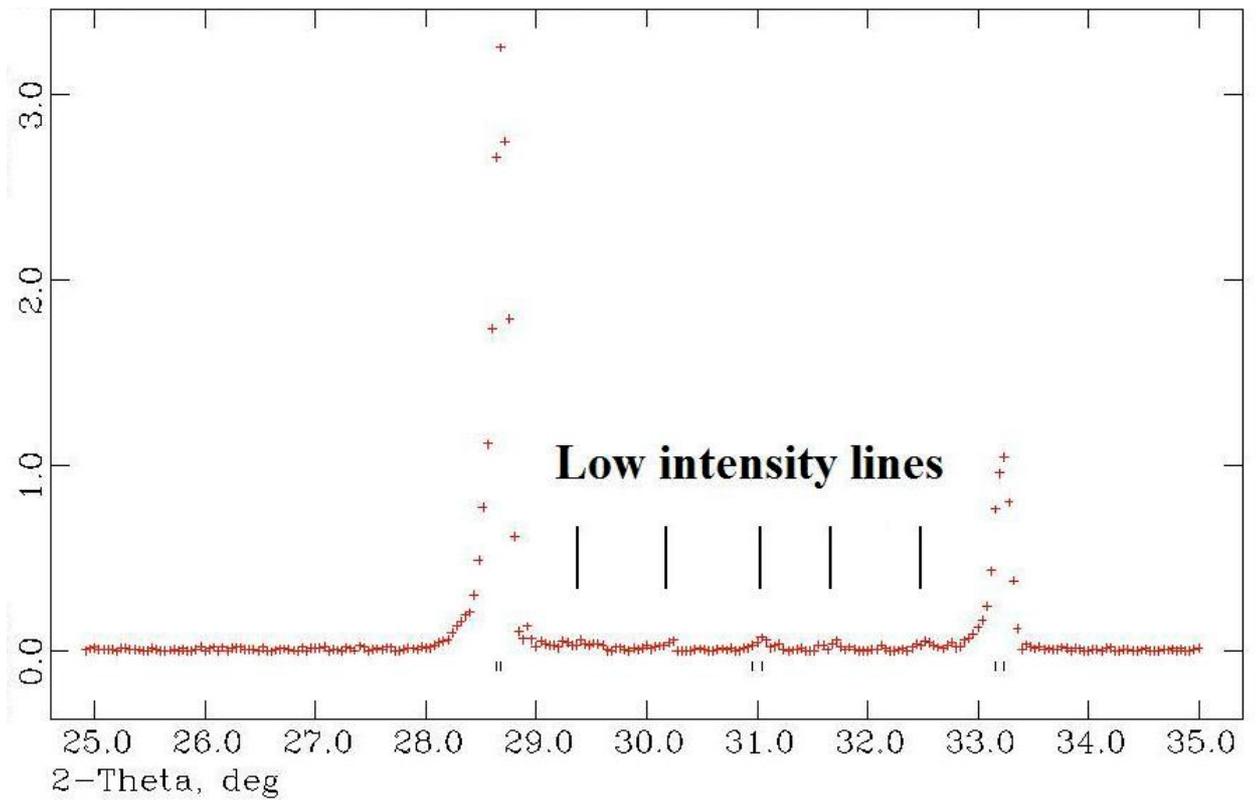
Figure 7.29 Diffraction pattern of Gd$_2$O$_3$ following 1 hour anneal at 1334ºC showing low-intensity reflections due to the monoclinic phase.

The pattern for Gd$_2$O$_3$ obtained after 1 hour in the Heraeus furnace at 1500ºC again appeared virtually identical to that prior to heating. As with the Carbolite furnace experiment, the same low-intensity reflections appeared around $2\theta = 30°$. In addition, there were also two low intensity reflections around $2\theta = 46.6°$ and $47.2°$. These are indicated in figure 7.30 below.
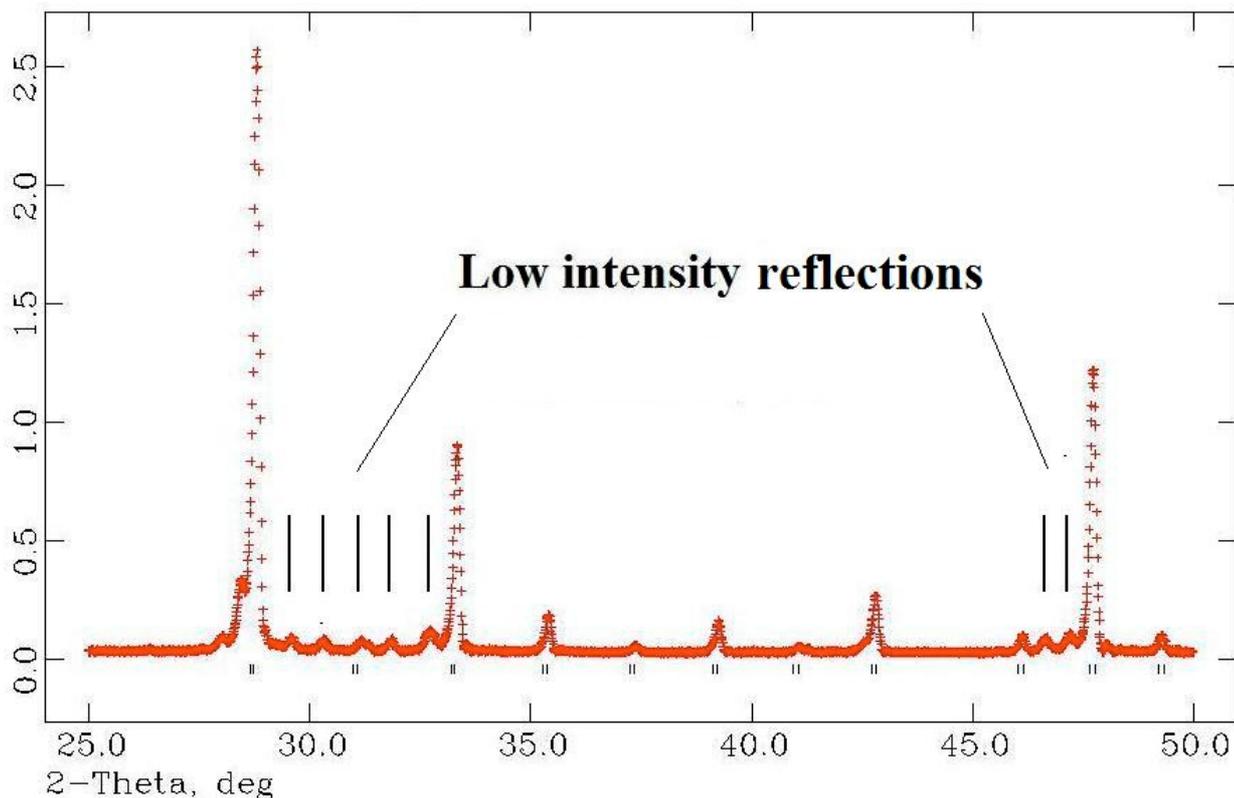
Figure 7.30 Diffraction pattern of Gd$_2$O$_3$ following 1 hour anneal at 1500ºC showing low-intensity reflections due to the monoclinic phase.

Because of the similarity with the europia cubic pattern it was assumed that these low intensity lines in the Gd$_2$O$_3$ XRPD patterns were due to the presence of some monoclinic phase. These 5 lines were run through CRYSFIRE to see if anything significant was found. None of the indexing programs found a solution that seemed reasonable and approximating to that of monoclinic Eu$_2$O$_3$. The 5 lines were then put into Chekcell and a set of calculated reflections generated from the monoclinic Eu$_2$O$_3$ unit cell parameters. These parameters were refined until the experimental and calculated lines converged. Thus a set of approximate unit cell parameters for monoclinic Gd$_2$O$_3$ were found, namely $a = 14.05$Å, $b = 3.52$Å, $c = 8.58$Å, $\beta = 100.19$º.

The pattern for Gd$_2$O$_3$ obtained after 7 hours' annealing at 1500ºC in the Heraeus furnace showed an almost complete conversion to the monoclinic phase. Figure 7.31 shows the original cubic pattern and the monoclinic pattern. The 4 lowest angle cubic lines still retained are marked. These lines were at $2\theta = 20.28$º, 28.73º, 33.23º and

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35.38°. Other reflections due to the cubic cell were also present at higher angles (2θ = 56.55°, 57.89°, 59.26°, 63.24°, 68.36°, 69.56°, 76.91° and 88.59°).
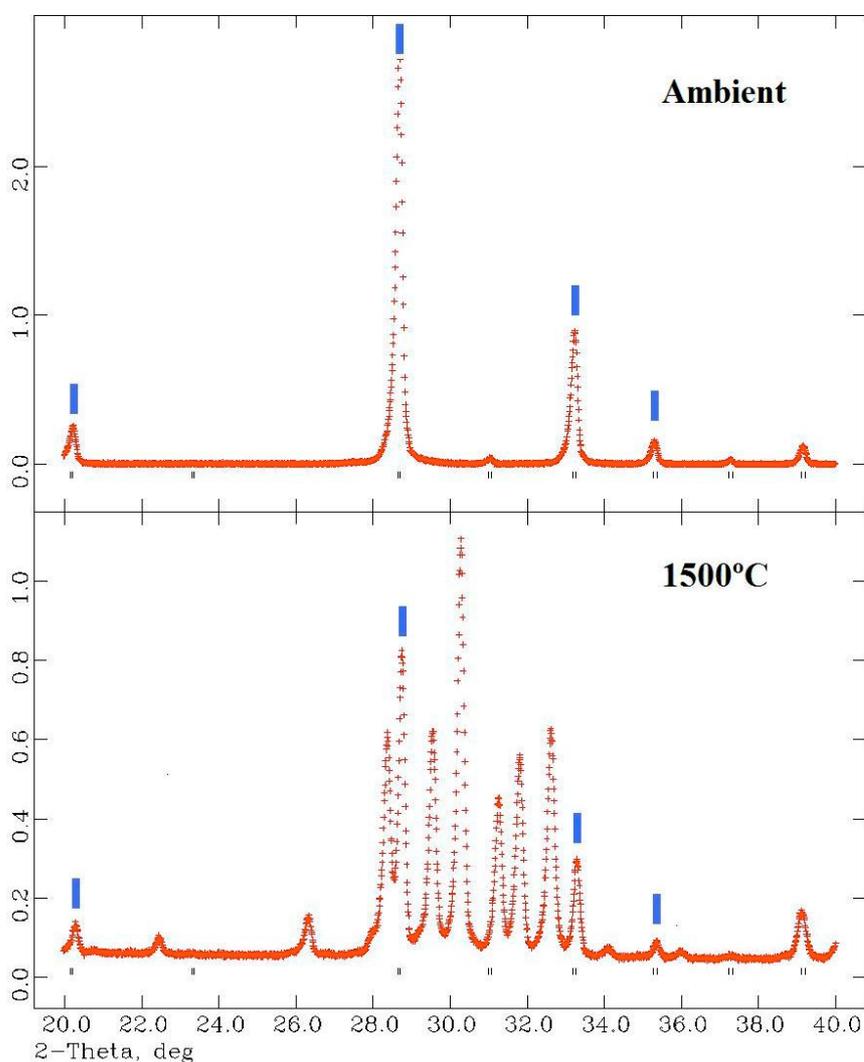
Figure 7.31 Cubic (upper image) and monoclinic (following 7 hour anneal at 1500°C) patterns for Gd_2O_3. The 4 marks indicate the cubic lines which were retained after annealing.

Indexing of the 7-hour annealed gadolinia pattern using CRYSFIRE/Chekcell was attempted, discarding the 4 cubic lines and allowing for a zero shift in the pattern of 0.2 degrees following the running of a quartz standard in the diffractometer. However, no results analogous to that of monoclinic europia were obtained. It was therefore decided to use the approximate unit cell parameters obtained above. These parameters proved too far from the solution for GSAS to converge. It was then decided to estimate the unit cell parameters of monoclinic Gd_2O_3 by looking at the known cell parameters for its

neighbours samaria, europia and terbia and interpolating to find those for gadolinia. Figure 7.32 shows this process for estimating the value of the *a* parameter, although in practice this process was repeated for the other unit cell parameters. A similar method has been applied for the determination of the lutetia cell (Sun *et al* 2007) although in this reference the cell of B-type Sm_2O_3 was used as the starting point.
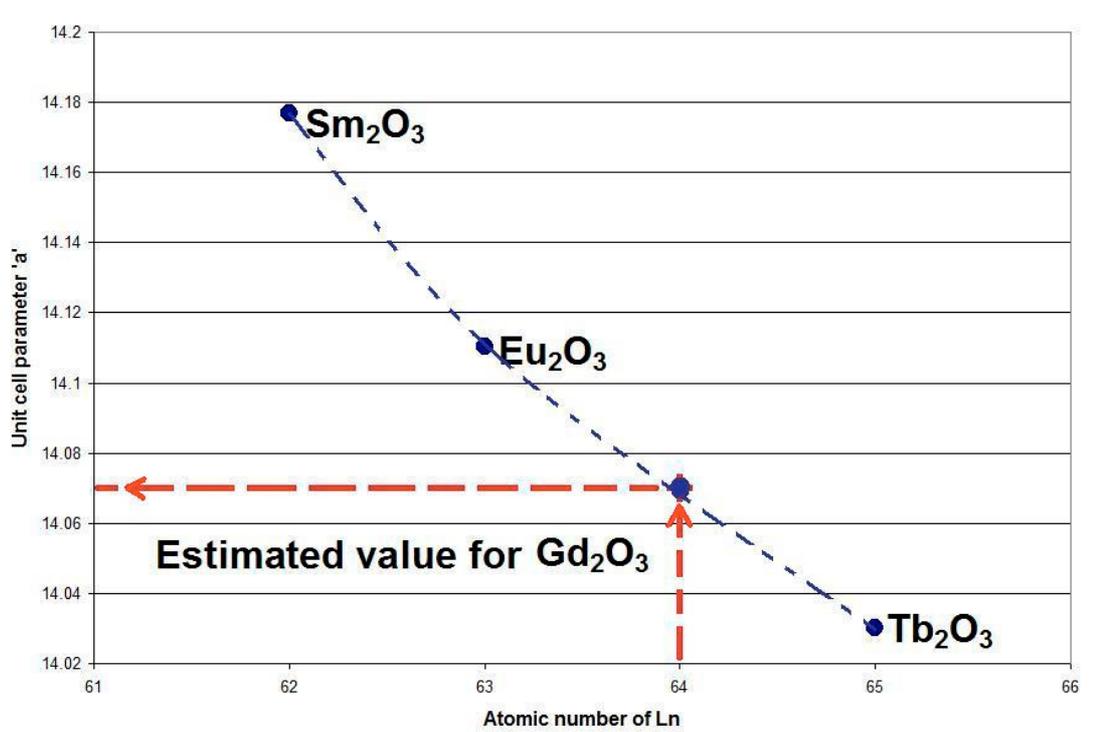
Figure 7.32 Estimation of unit cell parameter 'a' for monoclinic Gd_2O_3 by a method of interpolation.

The provisional unit cell parameters for monoclinic Gd_2O_3 were estimated at $a = 14.07$Å, $b = 3.57$Å, $c = 8.77$Å, $\beta = 100.07°$. It should be noted that although a and b are close to those estimated from the 1 hour heating data, the value of c is significantly higher.

Least squares refinement still left a discrepancy in intensity for the $2\theta = 30.06°$ peak (40$\underline{2}$ plane). The remainder of the peaks were well fitted. It was thought that the discrepancy might be explained by preferred orientation of the microcrystalline sample. To this end, the sample was reground and the pattern collected again. However, the pattern showed no change. This discrepancy was seen neither with the europia

monoclinic pattern nor the second gadolinia sample exposed to synchrotron radiation. There is no ambient phase peak in the same 2θ region that might cause superposition. The problem peak was therefore put down to preferred orientation that was not sufficiently ground out.

Analysis of the pattern from the refined phase fractions in GSAS showed there to be approximately 97% of the monoclinic phase and 3% of the cubic phase present.

Because of the significantly greater energy input required to force the conversion in gadolinia compared to europia, it was decided to repeat an XRPD pattern at a later date in order to determine if there had been any change in the phase fractions. The sample was analysed 5 months after annealing and found to contain the same proportion of B-type oxide.

Unlike sample (2), sample (8) Gd_2O_3 showed a complete conversion following the same time at what was believed to be the same temperature. Sample (2) was annealed in a cylindrical crucible with the open end exposed to the air. Sample (8) was annealed in the enclosed space of the DSC. It is likely that the temperature for sample (8) was slightly higher and not subject to the cooling effect of direct exposure to the atmosphere. The diffraction pattern (figure 7.26) shows distinct and narrow Bragg reflections characteristic of those generated using synchrotron radiation. Although the data was captured up to 149.99° of 2θ it was not possible to load the entire diffraction pattern into the relevant software due to the file size. Instead the characteristic region below 40° was chosen. To ensure there was nothing other than monoclinic phase present the entire diffractogram was loaded into a spreadsheet and compared against a calculated pattern. The patterns were found to correspond exactly, meaning that the sample had completely converted to the monoclinic phase. This is contrary to sample (2), where 100% conversion to the monoclinic phase did not occur.

7.2.4.3 Ytterbia

Heating the Yb_2O_3 sample for 1 hour in the Heraeus furnace produced virtually no change in the diffraction pattern. As with Gd_2O_3 there was a small change with the

appearance of low intensity lines around $2\theta = 30^{\circ}$, although this time they were considerably weaker than for gadolinia. This is to be expected, since increasing atomic number of the rare earth is accompanied by a sharp increase in the energy needed to make the phase transition.
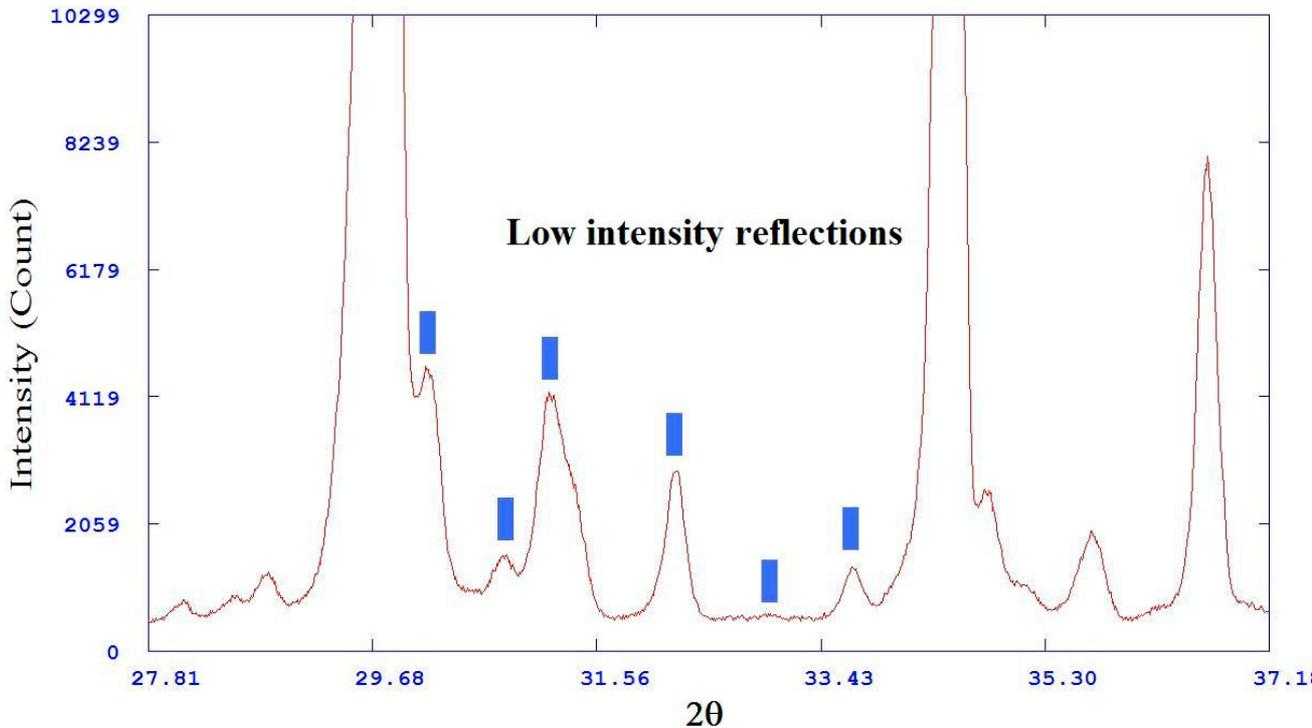
Figure 7.33 XRPD pattern of Yb₂O₃ post-heating to 1500ºC showing low-intensity reflections due to the monoclinic phase.

Because of the similarity with the Gd_2O_3 pattern in figure 7.20 (and the cubic europia pattern in figure 7.1) it was again assumed that the low intensity lines in the Yb_2O_3 pattern around $2\theta = 30^{\circ}$ were due to the presence of a monoclinic phase. These 6 lines were run through CRYSFIRE to determine if anything significant could be found. None of the software found a solution that seemed reasonable or approximated to that of monoclinic Eu_2O_3. The 6 lines were then put into Chekcell and a set of calculated lines generated from unit cell parameters extrapolated from monoclinic europia. The starting points were taken as $a = 13.75$Å, $b = 3.45$Å, $c = 8.5$Å and $\beta = 100.2^{\circ}$. These parameters were refined until the experimental and calculated lines converged. Thus a set of approximate unit cell parameters for monoclinic Yb_2O_3 were found, namely $a = 13.740(2)$Å, $b = 3.400(2)$Å, $c = 8.593(2)$Å and $\beta = 100.12^{\circ}$. The existence of this phase

is contrary to the phase diagram and also to recently published work (Guo, Harvey *et al* 2007), (Meyer *et al* 1995).

The pattern for Yb_2O_3 obtained post-heating for 7 hours in the Heraeus furnace again showed little conversion to the monoclinic phase. The same 6 monoclinic lines were visible around $2\theta = 30°$ but there was no increase in intensity relative to the other lines. Because of this no further work was carried out on the diffraction pattern.

Using the estimated unit cell parameters for ytterbia and assuming the atom positions to be the same as for gadolinia, analysis of the pattern from the refined phase fractions in GSAS showed there to be approximately 99% of the cubic phase and 1% of the monoclinic phase present.

The pattern for Yb_2O_3 obtained post-heating for 5 hours at 1800°C showed no conversion to the monoclinic phase. There was a 2-week delay between the annealing and the diffraction pattern being collected. It would be reasonable to assume that the material had converted at least as much as sample (3) in the furnace and possibly more because of the increased temperature. However, the monoclinic phase of ytterbia is obviously very unstable under ambient conditions. To show the change, the immediate recording of XRPD data under ambient conditions or, ideally, in situ XRPD, would be needed.

7.3 IN SITU HIGH TEMPERATURE XRPD

7.3.1 Praseodymia ramp in air

The purpose of this section was to identify the temperatures of the phase transitions within the range of the diffractometer with the intention of then carrying out the kinetic study detailed in 7.3.2. Sample (4) was heated in 25° steps from 25°C to 800°C and cooled back in 25°C steps to 125°C. At each temperature a diffraction pattern was recorded. The 33 XRPD patterns obtained from 25°C to 800°C are shown stacked together in the 3 images below.
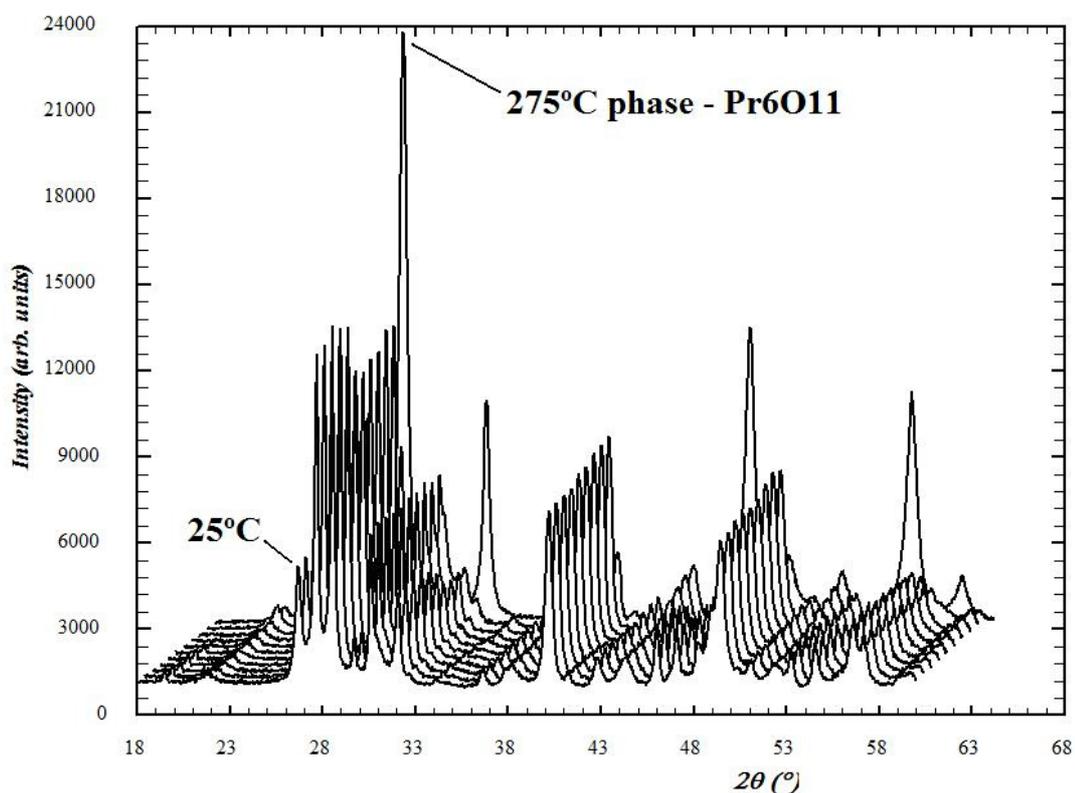
Figure 7.34 Praseodymia ramp 25ºC to 275ºC showing the appearance of the ceria-type β phase (Pr$_6$O$_{11}$) at 275ºC.

Figure 7.34 shows the sudden appearance of the β phase at 275ºC. Here the pattern corresponding to the mixed A and C-type phases transforms to the 5-peak pattern of the CeO$_2$ structure. This structure is represented in the phase diagram in figure 1.9 by a narrow vertical section to the bottom right. The 5 peaks were run through CRYSFIRE. However, the program was unable to index the XRPD pattern because of the small number of lines. GRAPHPRO returned the unit cell parameter as 5.476 Å. Full profile refinement using GSAS was carried out using the atom positions in the ICDD database reference 42-1121. The refined unit cell parameter was 5.4790(2)Å.
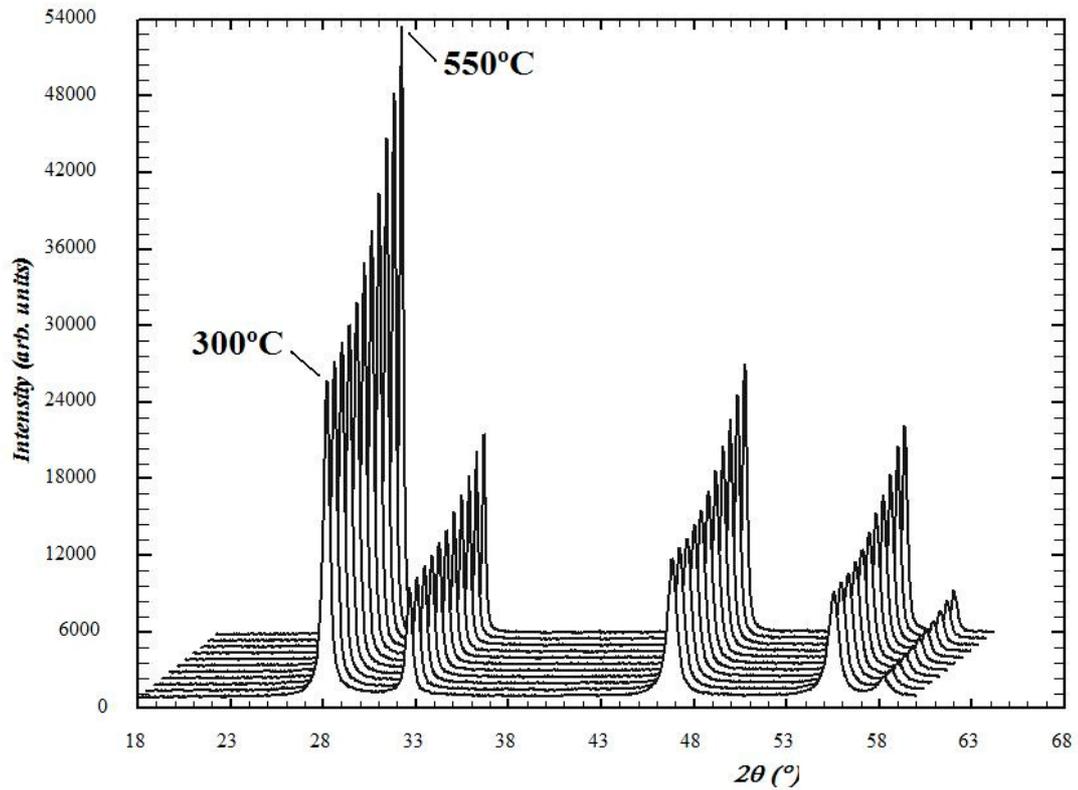
Figure 7.35 Praseodymia ramp 300ºC to 550ºC showing the ceria cell throughout.

Figure 7.35 shows no change throughout the temperature ramp other than an intensifying of the reflections. Although the phase diagram shows there are 3 phases in this range (the δ, ε and ζ phases), there was no indication of any structural change from the XRPD patterns. This is to be expected as the changes are solely due to the different oxygen compositions whilst still retaining the ceria-type cubic cell. The contribution to peak intensities from oxygen is small compared to that of praseodymium.
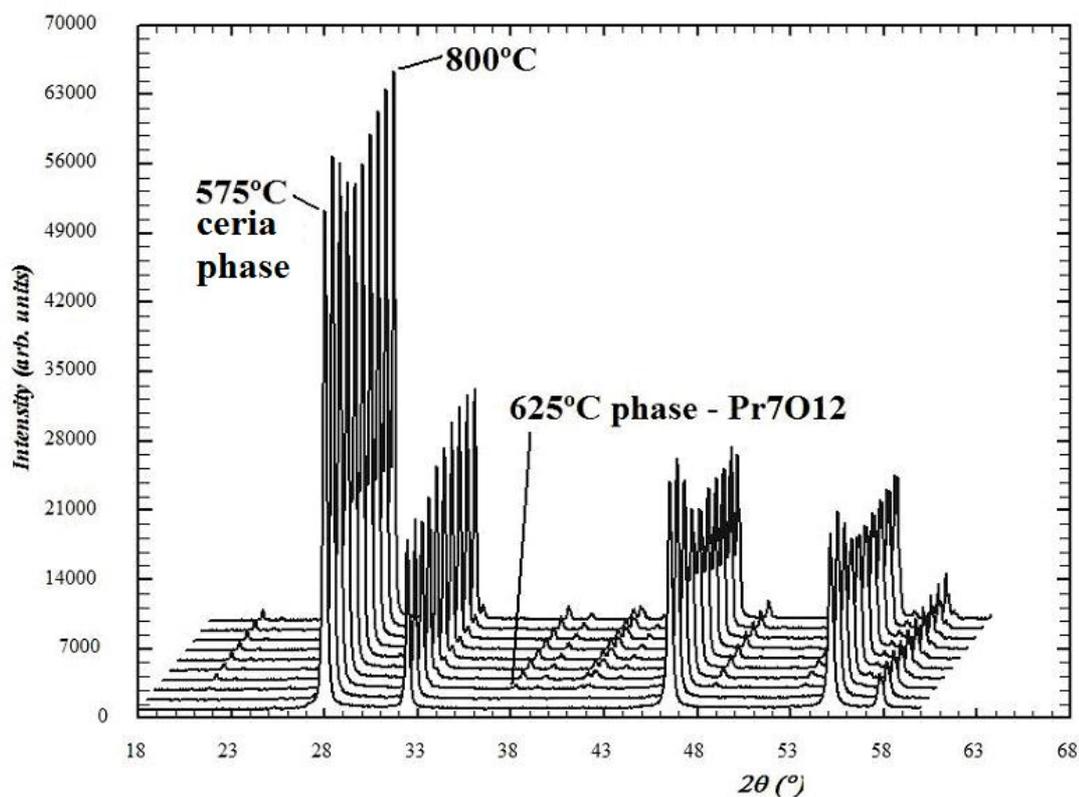
Figure 7.36 Praseosymia ramp 575°C to 800°C showing the appearance of the ι phase (Pr₇O₁₂) at 625°C.

It is not until 625°C that a new cell type is discernible in the diffractograms, where the ι phase slowly emerges over a series of patterns in figure 7.36. Its presence is indicated by the weak reflection present between the 5 stronger reflections already present. CRYSFIRE was unable to index the XRPD pattern of this new structure. Full profile refinement using GSAS was carried out using the atom positions in the ICDD database reference 7-0449. The refined unit cell parameters were $a = 10.3460(2)$Å and $c = 9.6430(2)$Å, space group R-3.

The diffraction patterns for both the β and ι phases are shown in figures 7.37 and 7.38.
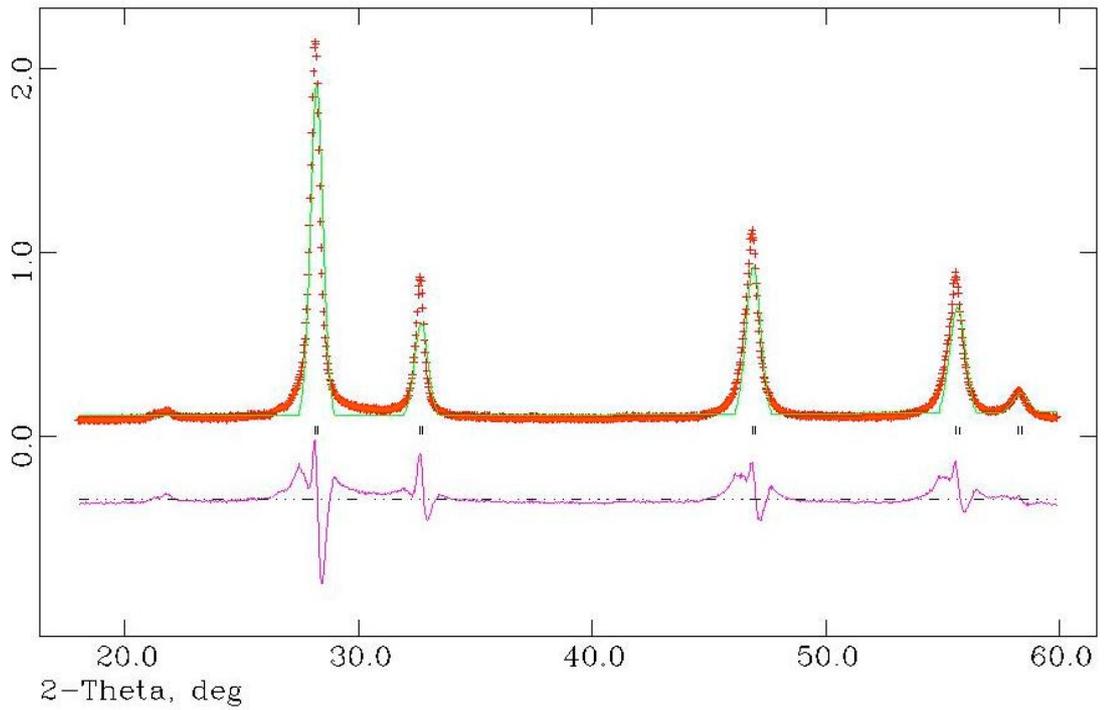
Figure 7.37 Final stage of refinement of the β phase (Pr$_6$O$_{11}$) of praseodymia.
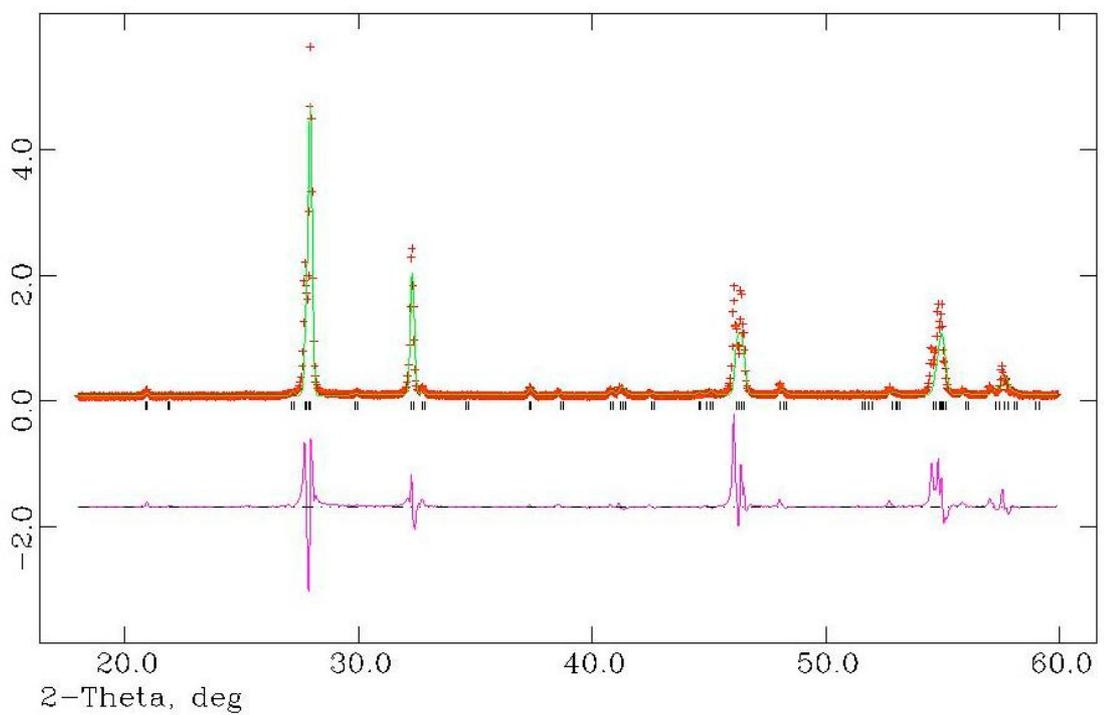
Figure 7.38 Final stage of refinement of the ι phase (Pr$_7$O$_{12}$) of praseodymia.

The 28 XRPD patterns obtained on cooling back from 800ºC to 125ºC are shown stacked together in the 2 images below.
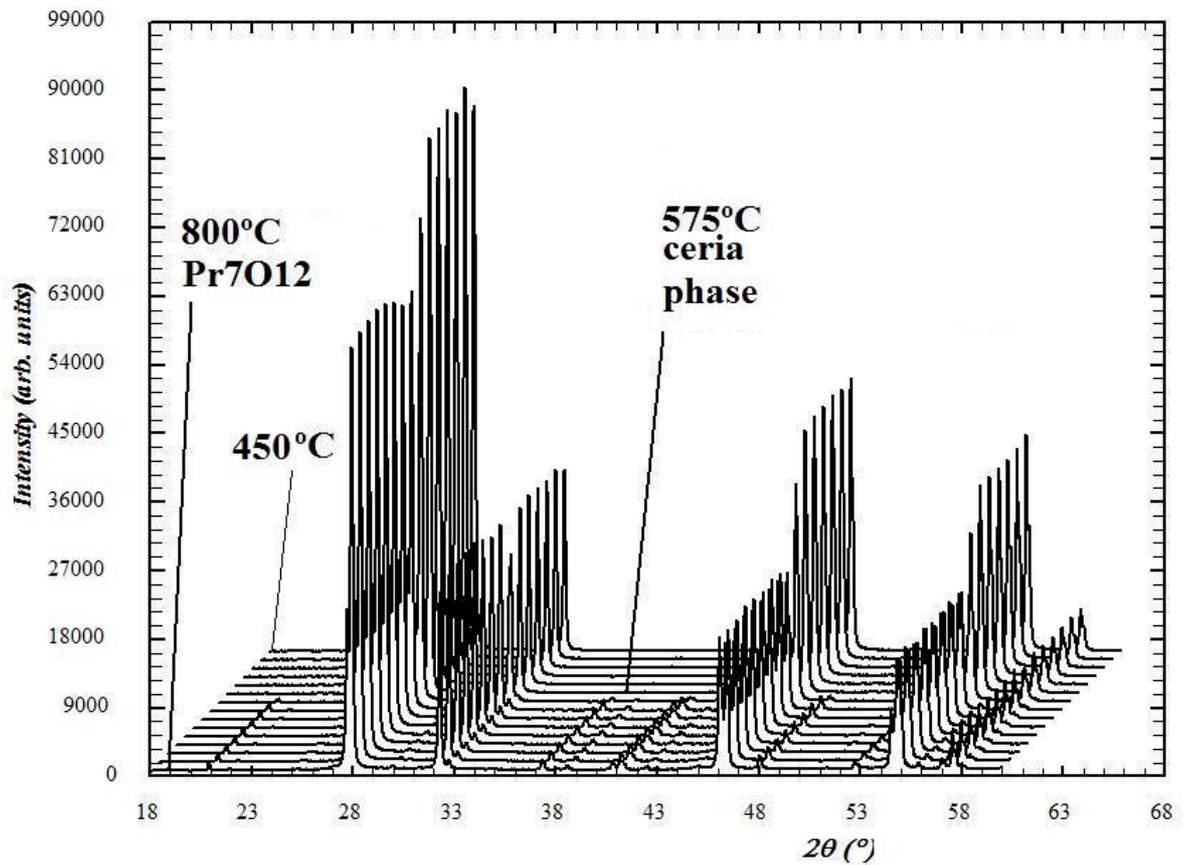
Figure 7.39 Praseodymia ramp 800ºC to 450ºC showing the loss of the ı phase of Pr₇O₁₂ at 575ºC.

Figure 7.39 shows that on cooling the sample back from 800°C, the *ı* phase which had appeared at 625°C when the temperature was ascending disappeared at 575°C. This marks the point where the conversion back to the ceria cell occurred. More detailed examples of hysteresis in the Pr-O system will be shown in chapter 8.
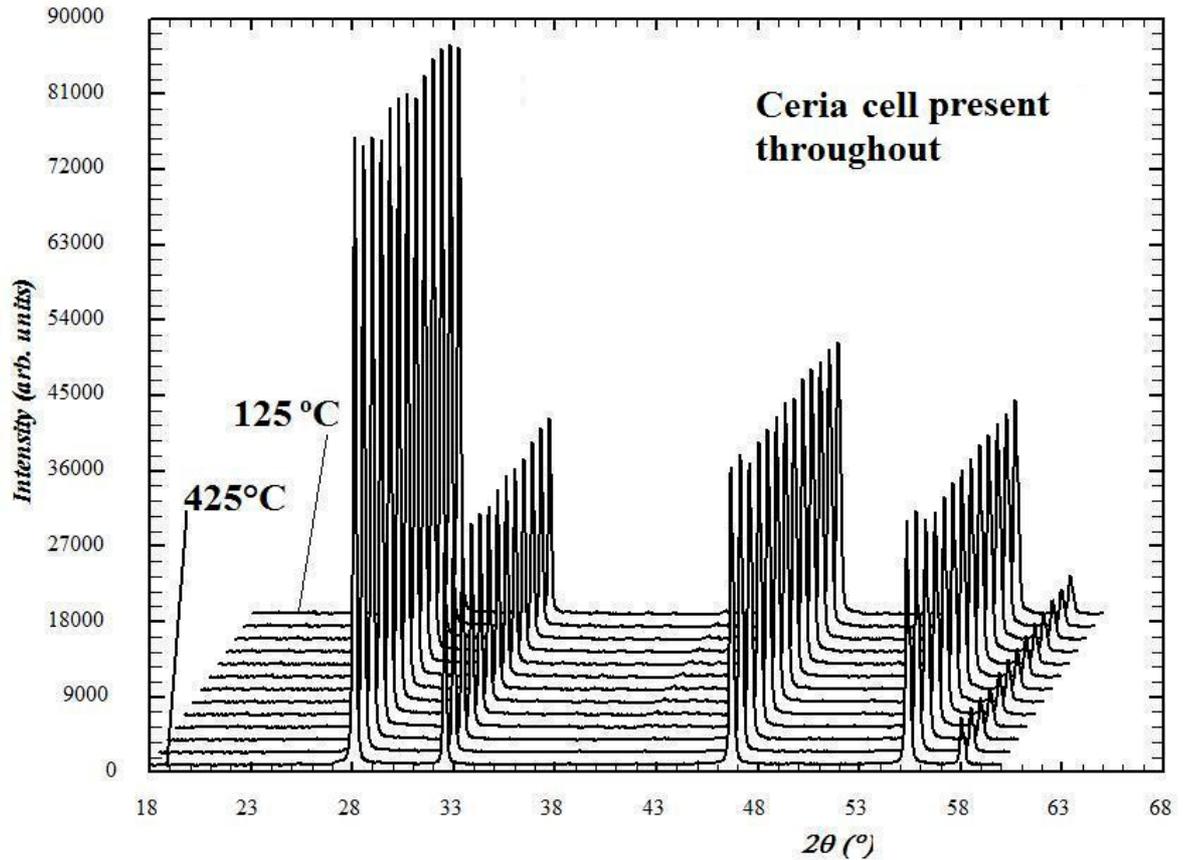
Figure 7.40 Praseodymia ramp 425ºC to 125ºC showing the ceria cell throughout.

Figure 7.40 shows that further cooling showed no change in the XRPD pattern i.e. the ambient temperature phase did not appear below 300°C. This echoes findings with europia and gadolinia; some high-temperature phases are metastable.

7.3.2 Praseodymia isothermal holds in air - conversion from Pr_2O_3 to Pr_6O_{11} at 275 °C

Now that the transition temperature for formation of the β phase had been established at approximately 275°C it was possible to perform a series of isothermal holds close to this temperature to observe how fast the reaction proceeded with temperature.

7.3.2.1 Peak heights and intensities

Figure 7.41 shows an example of the ambient temperature phase transforming into the β-phase over a period of 45 minutes.
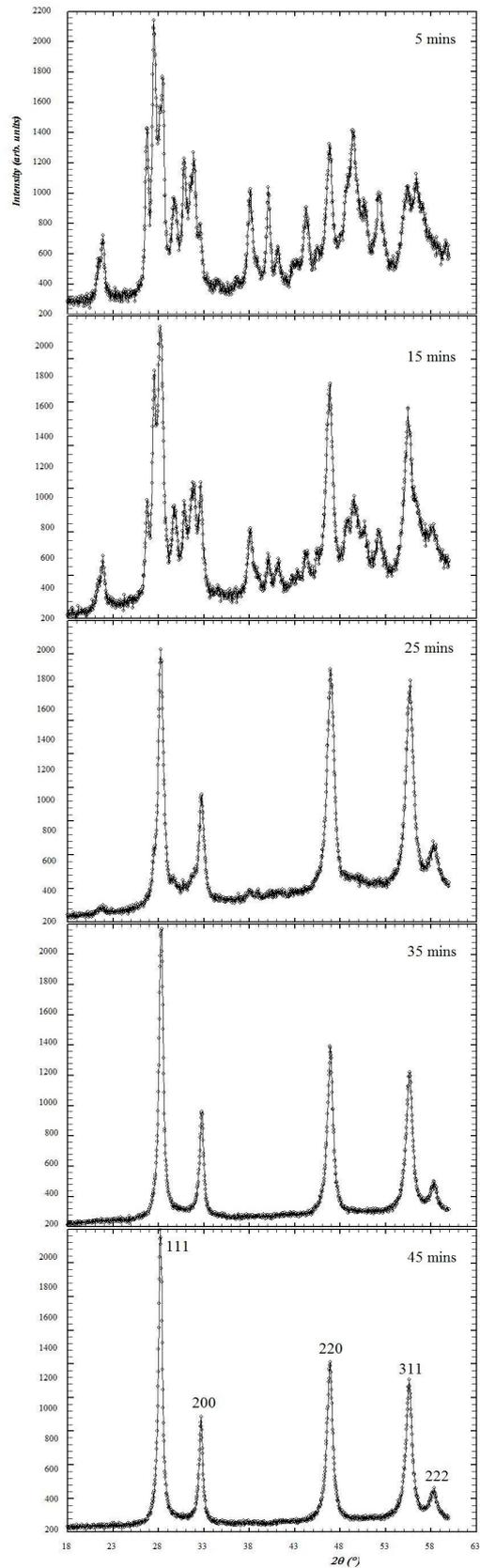
Figure 7.41 The five Bragg peaks of the β phase emerging from the ambient mixed phase during the 250 ℃ isothermal hold.

The diffraction patterns in figure 7.41 clearly show the 5 peaks of the high-temperature phase emerging from the pattern of the ambient mixed phase. Two characteristic peaks were chosen for analysis. These were at 47.2° (corresponding to the 220 plane in the β phase) and 41.4° (the 012 plane in the ambient cubic phase). The integrated intensities of these peaks were recorded across each isothermal hold and the fractional changes in the peaks plotted against time. The following chart illustrates the degree of conversion to the β phase as measured by the increase in intensity of the 47.2° peak.
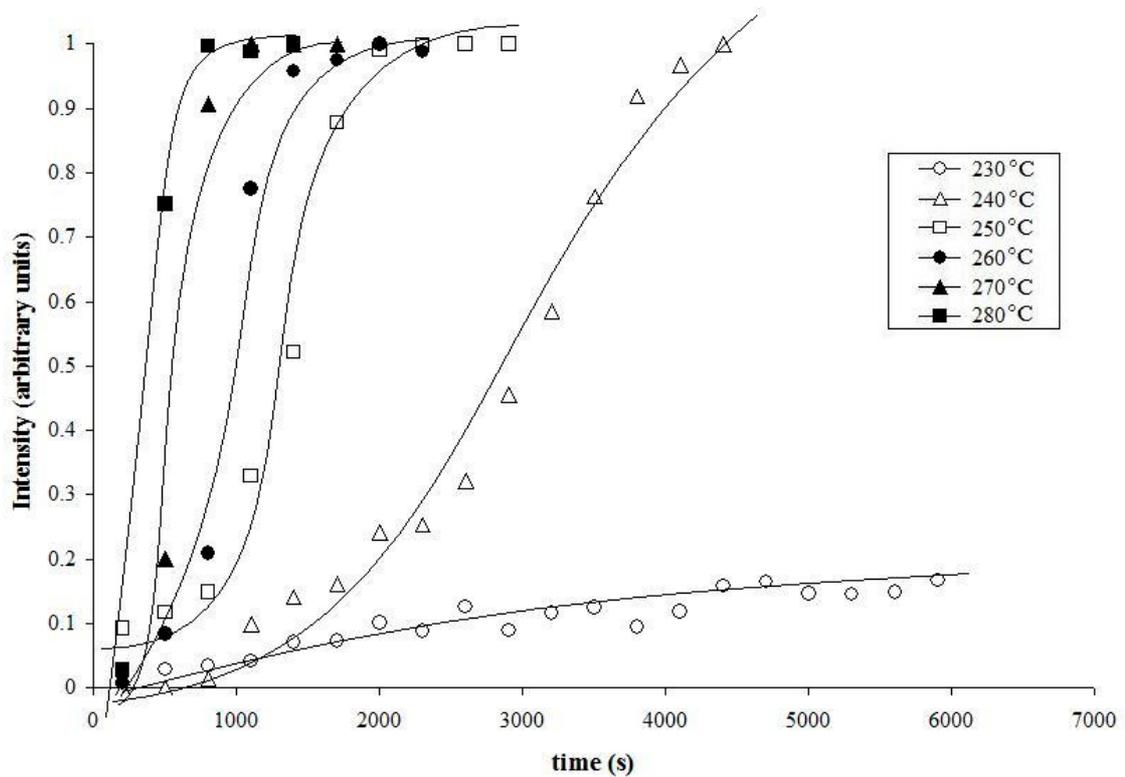
Figure 7.42 Conversion against time for Pr_2O_3 to Pr_6O_{11} phase change using the increase in intensity of the 47.2° (β phase 220 plane) peak.

7.3.2.2 Shrinking Sphere model

The fractional conversions for the 230°C holds were discarded as there were found to be anomalies in the data due to operational error. Use of the Shrinking Sphere model on the remaining holds at 240°C, 250°C, 260°C, 270°C and 280°C gave the set of kinetic isotherms in figure 7.43.

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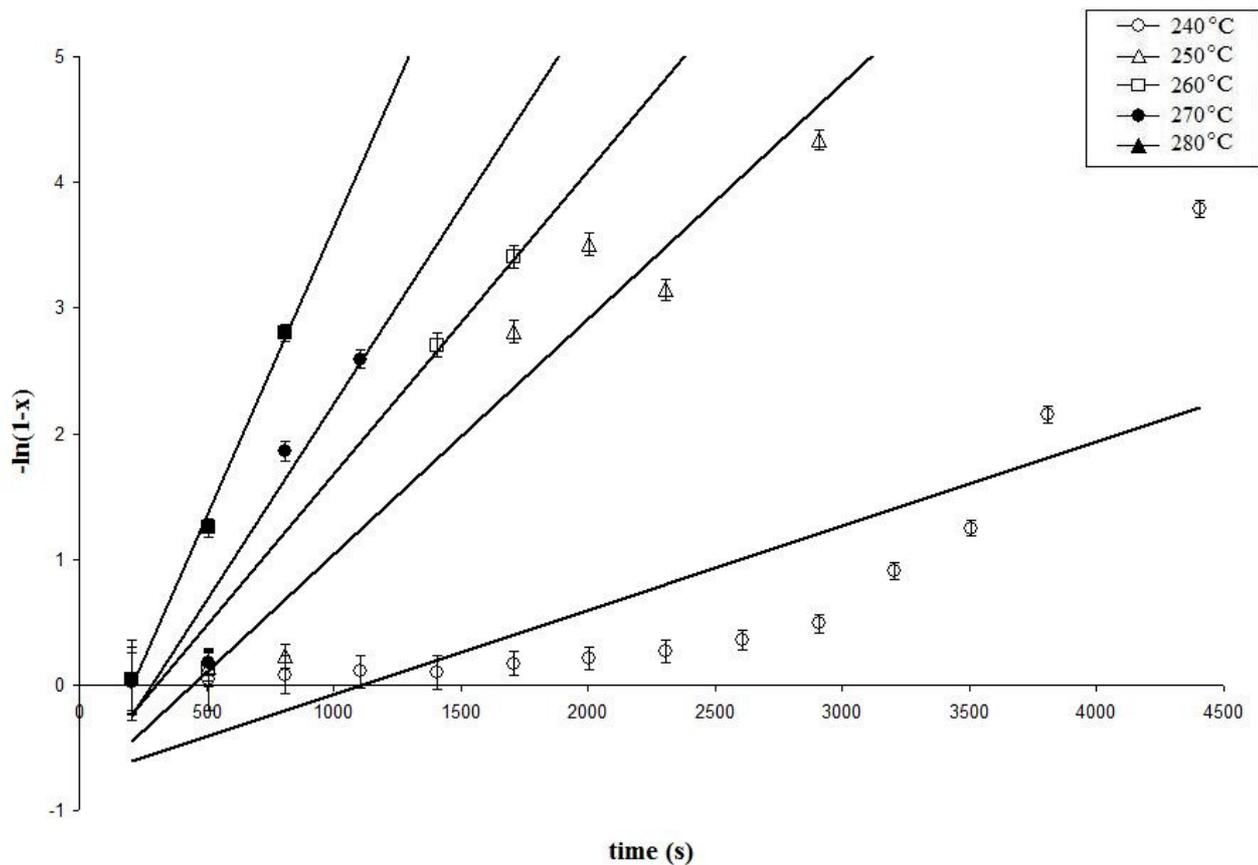
Figure 7.43 Shrinking Sphere kinetic isotherms for the 47.2° (β phase 220 plane) peak.

Use of the data in the above chart gave the following set of values for the rate constant, *k*.

Temp (°C)	k (s^{-1})
240	7×10^{-4}
250	3.2×10^{-3}
260	2.8×10^{-3}
270	7.9×10^{-3}
280	9.7×10^{-3}

Table 7.17 Values of the rate constant, k, for the 47.2° (β phase 220 plane) peak.

A plot of ln *k* against reciprocal temperature is shown below.
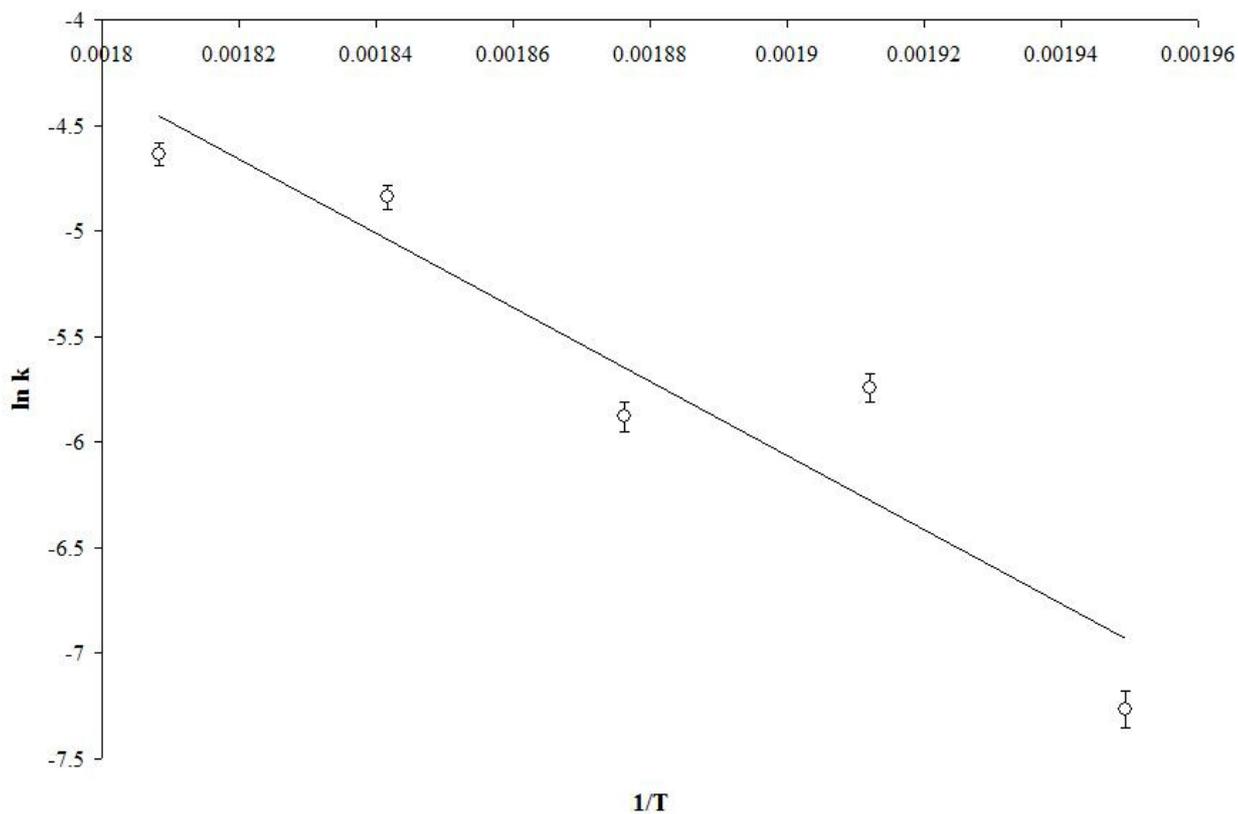
Figure 7.44 Plot of ln k against 1/T for the 47.2º (β phase 220 plane) peak.

Further analysis of the above data generated value of -146(2) kJ.mol^{-1} for the activation energy.

7.3.2.3 JMAK model

Starting with the same fractional conversion data as in 7.3.2.2, use of the JMAK model gave the following double log plot.
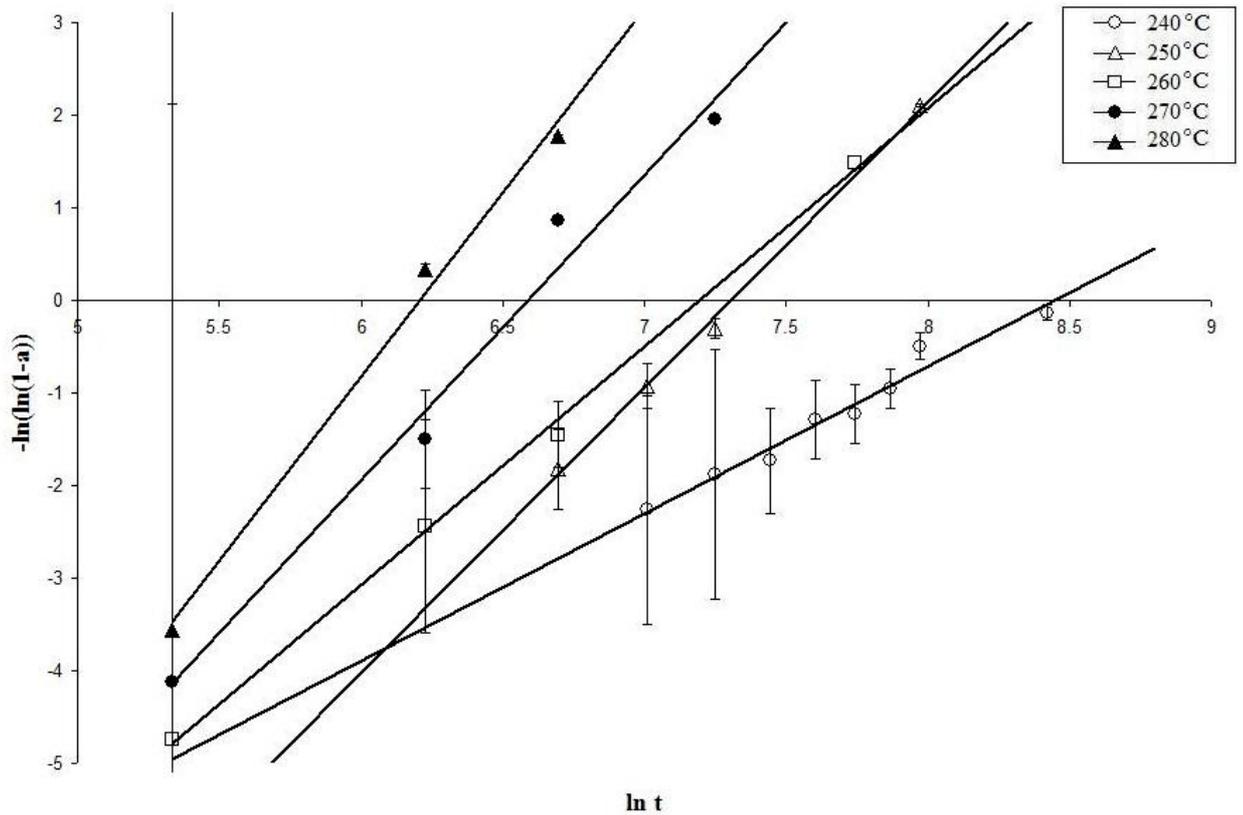
Figure 7.45 JMAK kinetic isotherms for the 47.2° (β phase 220 plane) peak.

Use of the data in the above chart gave the following set of values for the rate constant, k and Avrami exponent, n.

Temp (°C)	K (s⁻¹)	n
230	Not able to determine	Not able to determine
240	2.972×10^{-7}	1.80(59)
250	1.68×10^{-10}	3.08(25)
260	9.182×10^{-9}	2.57(7)
270	3.777×10^{-10}	3.29(6)
280	1.308×10^{-9}	3.24(11)

Table 7.18 Values of the rate constant and Avrami exponent for the 47.2° (β phase 220 plane) peak.

JMAK data obtained from accurately recorded data should yield a series of plots in figure 7.45 with similar gradient, corresponding to the Avrami exponent. In turn, the plot in figure 7.46 should be a downward sloping line. Because of the lack of data (only 5 data points) and the erratic spread of Avrami exponents in table 7.18 it was decided to

take a practical approach and only use the data giving similar gradients in figure 7.45. The relevant temperature holds were 250ºC, 270ºC and 280ºC. A plot of ln k against reciprocal temperature is shown below.
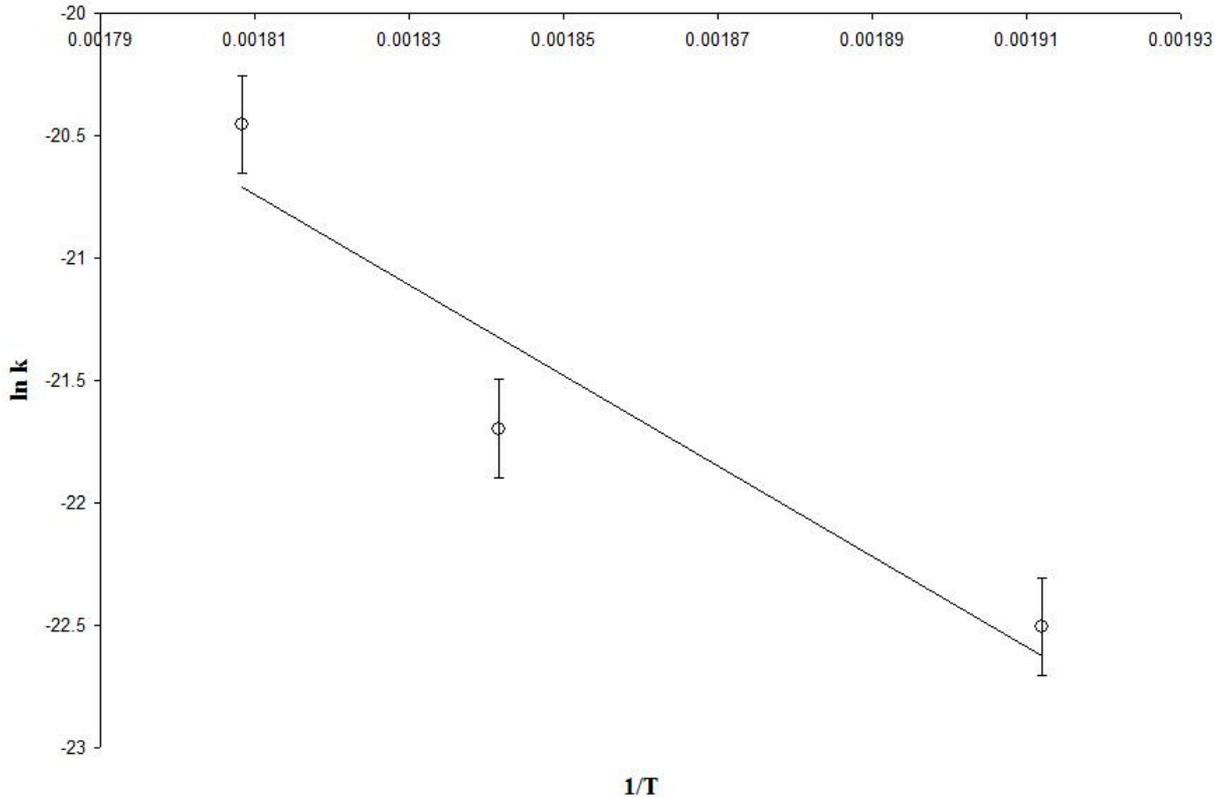
Figure 7.46 Plot of ln k against 1/T for the 47.2º (β phase 220 plane) peak.

Further analysis of the above data generated a value of -154(2) kJ.mol^{-1} for the activation energy.

Figure 7.42 clearly shows that the isothermal hold at 230ºC was not long enough for significant conversion to take place. As a result of this, the data was of no use in determining the Avrami exponent. The 240ºC data does not level out, meaning that 100% conversion did not occur. Again, this meant that the value for the Avrami exponent could not be deemed accurate. The remaining 4 values for the Avrami exponent do show some agreement, although had other holds been possible, perhaps at intermediate temperatures eg 245ºC, 255ºC etc, the value for the activation energy might have been improved. The JMAK model is useful in providing the dimensionality information via the Avrami exponent, but to obtain it we must effectively take the log

of both sides of the Shrinking Sphere equation. The Shrinking Sphere model plots $-\ln(1 - x)$ against t whereas the JMAK model plots $\ln(-\ln(1 - x))$ against $\ln t$. In taking this secondary log, significant error is introduced into the working and therefore into the values for the Avrami exponent and activation energy. To counter this, it would be useful to record XRPD patterns more often. This would improve the kinetic isotherms and hopefully the values for the above quantities.

A summarised set of results, including that for the 41.4º peak, is given in the table below. The values for the activation energy obtained by both models for the 47.2º peak are close. Encouragingly, they correspond to the value of $-149(10)$ kJ.mol^{-1} for the 40.1º peak, where it had been assumed that the kinetics attributable to a collapsing peak in the XRPD pattern would be the same as that for a growing peak.

Peak	Phase	Method	EA (kJ.mol^{-1})	n
41.4º	Ambient hexagonal	Shrinking sphere	-149(10)	N/A
47.2º	High temp cubic	Shrinking sphere	-146(2)	N/A
47.2º	High temp cubic	JMAK	-154(2)	3.05(7) avg

Table 7.19 Values for activation energy for the $\phi \rightarrow \beta$ transition in Pr-O.

Referring to table 4.1, the value of n being between 3 and 4 indicates that the product phase propagates three-dimensionally from existing nucleation sites in the reactant material.

7.3.3 Praseodymia quench in air

The ι phase, which appeared at 625ºC when the temperature was ascending, was retained up to the maximum temperature reached of 800ºC. On quenching, the ceria phase was retained at ambient temperature as the β form.

7.3.4 Change in unit cell parameter with temperature

The temperature ramp in 7.3.1 showed 2 distinct changes to the XRPD pattern. At about 275°C there was a significant change, corresponding to the mixed A and C-type

phase converting to Pr_6O_{11}. At 625°C there was a more subtle change in the pattern with Pr_6O_{11} converting to Pr_7O_{12}. With increasing temperature there is an associated thermal expansion of the crystal lattice, indicated by a small shift in the positions of the Bragg reflections. This phenomenon is often used as a means of measuring temperature in situ when XRPD data is being collected at high temperature. In such a case, a known material such as platinum is introduced to the sample and the shift in its Bragg peaks used to determine temperature. The following table shows the values for the unit cell parameters between 275°C and 800°C, obtained by observing the change in the position of the 111 reflection.
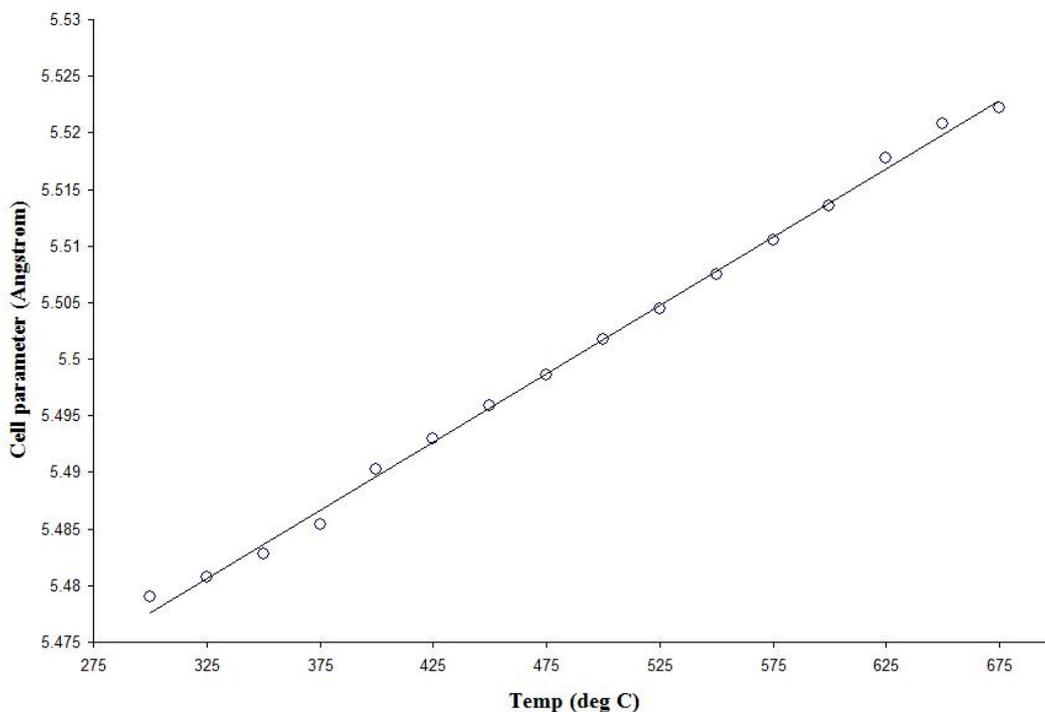
Figure 7.47 Variation in unit cell parameter with temperature for Pr_6O_{11}. Error bars are within the data points.

Figure 7.47 shows a linear correlation between unit cell parameter and temperature.

7.4 COMPARISON WITH OTHER WORK

The study of the lanthanoid oxides is a long and well-established tradition and there is a vast amount of data in the available literature. The crystal structures of the sesquioxides are well known and they are in general agreement with the phase diagram in figure 1.5.

However, there are notable exceptions. The phase diagram does not indicate that high temperature modifications exist at ambient temperature. This work has shown that Sm_2O_3, Eu_2O_3 and Gd_2O_3 can all persist under ambient conditions. Additionally, high-temperature modifications exist which are not indicated in the diagram as existing at all, notably Er_2O_3 and Yb_2O_3, and may be quenched to ambient temperature.

Historically, there has been limited kinetic work done on the Pr-O system, the bulk of the data on the lanthanides lying with the oxides of neodymium to gadolinium. The main sources of XRPD data are Stecura and Ainscough, whose data is presented in table 7.20.

Oxide	Ambient phase	Reaction	EA (kJ.mol^{-1})
Nd_2O_3	Cubic	C-type $\rightarrow$ A-type	502[1]
Sm_2O_3	Cubic	C-type $\rightarrow$ B-type	628[1]
Eu_2O_3	Cubic	C-type $\rightarrow$ B-type	691[1]
Eu_2O_3	Cubic	C-type $\rightarrow$ B-type	493[2]
Gd_2O_3	Cubic	C-type $\rightarrow$ B-type	787[1]

Table 7.20 Activation energies for the lanthanide oxides.
[1] (Stecura 1966). [2] (Ainscough et al 1975)

The value for the activation energy of the $\phi \rightarrow \beta$ transformation in praseodymia is considerably lower. There is correlation between the 2 values obtained using the increase in height of the 47.2° Bragg reflection in the product phase (-146(2) kJ.mol^{-1} obtained via a shrinking sphere model and -154(2) kJ.mol^{-1} obtained via the JMAK model). The value obtained by looking at the fall in the 41.4° Bragg reflection in the reactant phase (-149(10) kJ.mol^{-1}) corresponds to the former two values, indicating the the assumption in its derivation was correct i.e. it is possible to use changes in either reactant or product peaks to obtain the same result. In addition to their closeness, the three values are relatively small when compared with the much higher values for the heavier oxides. The kinetic data obtained via XRPD will be discussed further in chapter 8 alongside the results obtained from DSC-TG both historically and in this work.

8 RESULTS FROM DIFFERENTIAL SCANNING CALORIMETRY

This chapter contains all the DSC work carried out on PrO_x. The work had five aims, namely:

(i) to identify phase changes in the system;

(ii) to perform kinetic measurements where possible;

(iii) to match phase changes against the published phase diagram;

(iv) to note any discrepancies between this work and the phase diagram;

(v) and to determine the extent of degradation of the material in air.

8.1 FULL RANGE DSC-TG IN NITROGEN

The results obtained from sample (4) using the full temperature range (up to 1550°C) of the instrument are given in the following 4 images.
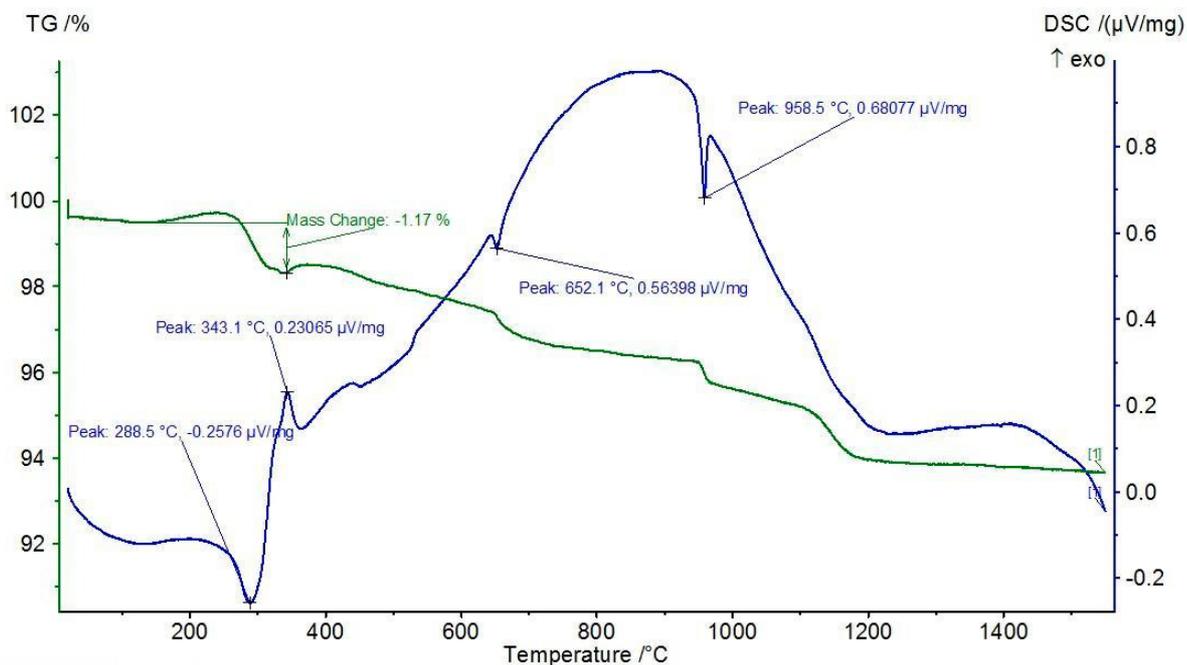
Figure 8.1 DSC-TG recorded on sample (4) Pr_2O_3 from 20°C to 1550°C at 10K/min under nitrogen.
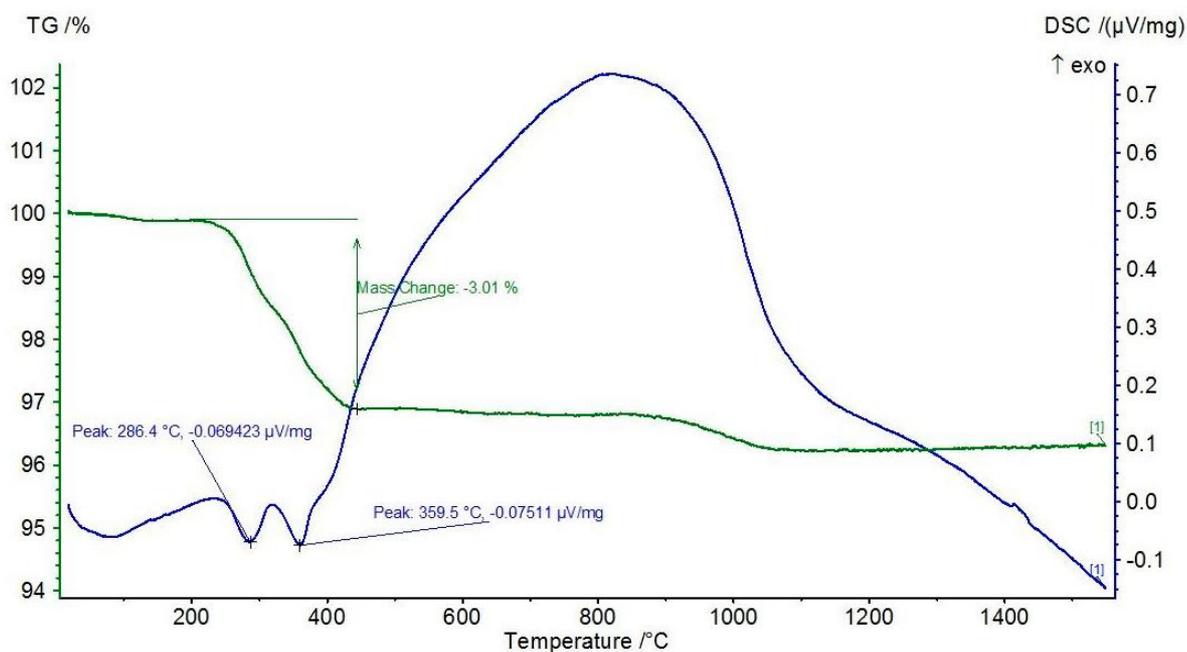
Figure 8.2 DSC-TG recorded on sample (4) Pr$_2$O$_3$ from 20°C to 1550°C at 10K/min under nitrogen. 2nd attempt, showing greater mass loss compared to figure 8.1.

The phase diagram for praseodymium sesquioxide (figure 1.5) shows only 2 structures: the cubic C form and the hexagonal A form. The transition temperature from one form to the other is not well defined in the diagram but appears to be around 500°C. Therefore a deflection was expected to be seen in the DSC around this temperature. However, this was not observed. Looking at the above images, there were two deflections between 280°C and 360°C and a large and broad peak after this temperature. Figure 8.1 shows deflections at 288.5°C, 343.1°C, 652.1°C and 958.5°C; the deflection at 288.5°C is accompanied by a small mass loss of 1.17%. Figure 8.2 still shows 2 deflections between 280°C and 360°C, but the other peaks present in figure 8.1 are absent, the remainder of the DSC line having become a large hump. The mass loss has now increased to 3.01%. The broad peak in all of figures 8.1 to 8.4 was not explainable in terms of the deflections expected from the phase diagram and a machine fault was suspected. What was interesting to note was that the sample removed from the DSC was no longer pale green but red-black, indicating that oxidation may have occurred. The phase diagram for the praseodymium-oxygen system (figure 1.9) was consulted. The diagram indicates that the hexagonal θ phase (sesquioxide) exists above 800°C, although in chapter 7 it has been established by XRPD that it can exist at

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ambient temperature. It was at first surprising to find that the sesquioxide was not retained on heating; it was assumed that the cubic ϕ phase present in the sample would be converted to hexagonal, leaving only the θ form. That this did not occur gave an indication of the complex nature of the Pr-O system and the readiness of praseodymium to undergo oxidation, even using a nitrogen atmosphere. That the oxidation occurs at a low temperature and was not prevented by the protective and purge gases indicated that the reaction had low activation energy. This was confirmed by the kinetic work in Chapters 7 and 8.

The conversion to the β phase was identified as a possible explanation for the deflections between 280°C and 360°C. The Pr-O phase diagram indicates a temperature of about 275°C for this change, which is in agreement with the DSC results. However, oxidation of Pr_2O_3 to Pr_6O_{11} would result in a mass increase of 3.2%, not a mass loss. It was believed that any mass increase was being masked by a larger loss, resulting in a net loss on the TG. Pr_2O_3 is known for absorbing carbon dioxide and water from the air (Anderson and Gallagher 1963). The possibility of mass loss due to the release of bound water or carbon dioxide was considered. The initial sample (4) came sealed in a glass ampoule and between the initial XRPD pattern and one taken 2 months later there was some change, albeit both cubic and hexagonal phases were still readily discernible. The 3.2% increase in mass due to oxidation would be swamped by the loss of, say, a fraction of water or carbon dioxide. Additionally, the TG in figures 8.1 and 8.2 do not show agreement in mass loss; this may be due to the sample degrading over time.

To investigate the mass loss, a further 2 runs were carried out on sample (4). This time the sample was pre-heated prior to using the DSC with the intention of driving off any absorbed gas but without inducing any oxidation or phase change.
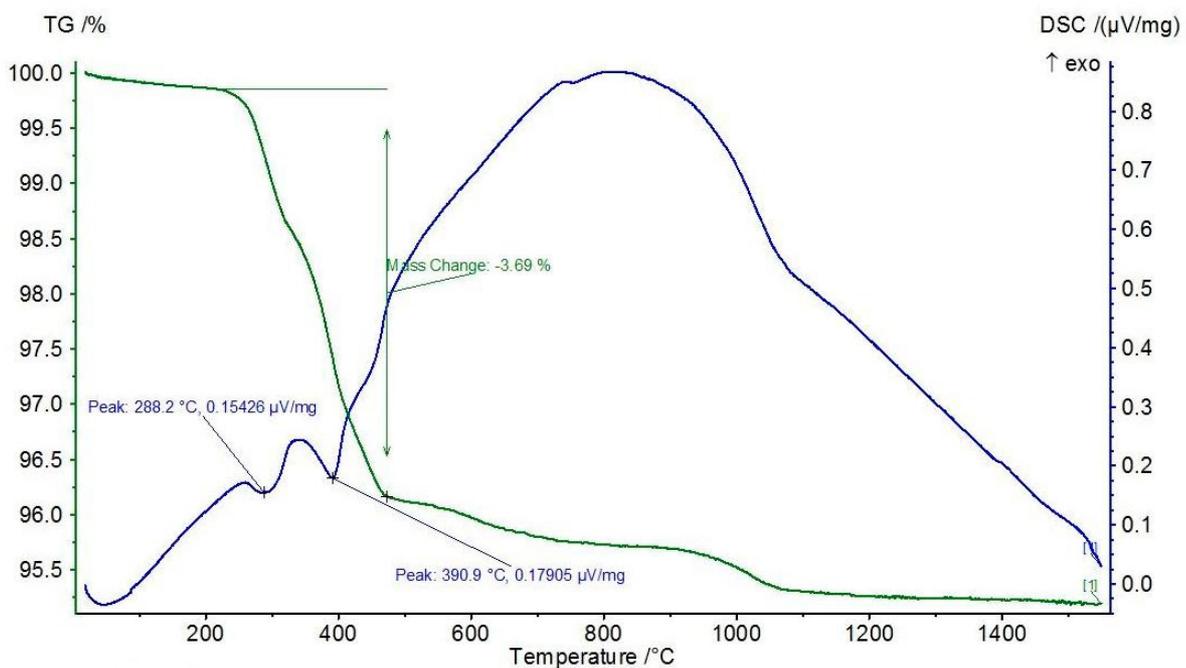
Figure 8.3 DSC-TG recorded on sample (4) Pr₂O₃ from 20℃ to 1550℃ at 10K/min under nitrogen following heating at 170℃ for 10 minutes.
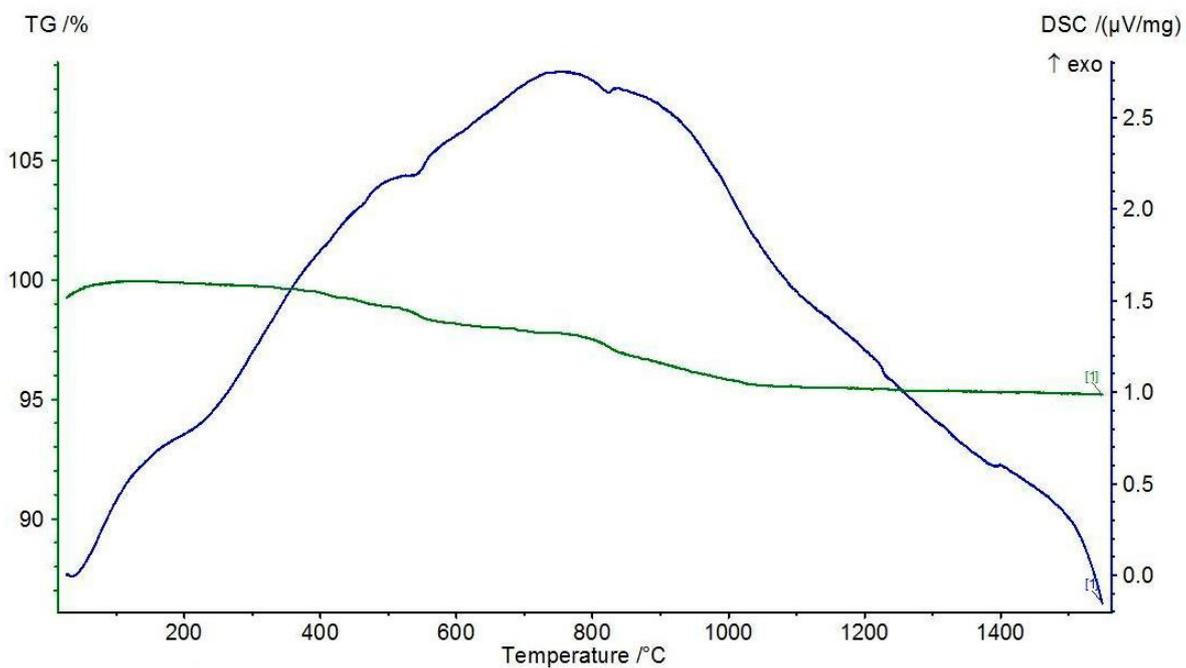
Figure 8.4 DSC 4 recorded on sample (4) Pr₂O₃ from 20℃ to 1550℃ at 10K/min under nitrogen following heating at 380℃ for 30 minutes.

Figure 8.3 shows 2 deflections between 280°C and 400°C. As with figure 8.2 the other deflections are absent, the remainder of the DSC plot having become a large hump. The mass loss has now increased a small amount to 3.69%. Figure 8.4 shows that the deflections between 280°C and 400°C have disappeared, although 2 peaks have appeared at 516°C and 822°C which may correspond to those in figure 8.1, although they have appeared at much lower temperatures. The mass loss has now dropped to below 0.5%.

The results following pre-heating indicate two properties of θ phase Pr_2O_3. Firstly, heating the sample to 170°C is not hot enough to drive off any bound gas. It may be that heating for an extended period at this temperature would cause a slow release of gas, but such facilities were not available. Secondly, the oxidation and the gas loss occur at the same point. It may be the case that the structural change from the hexagonal θ phase to the cubic ceria structure forces the release of gas from the lattice.

Following these unexpected results and to determine whether or not there were instrumental problems, the sample was run on a Mettler Toledo DSC. The resultant DSC-TG is shown in figure 8.5.
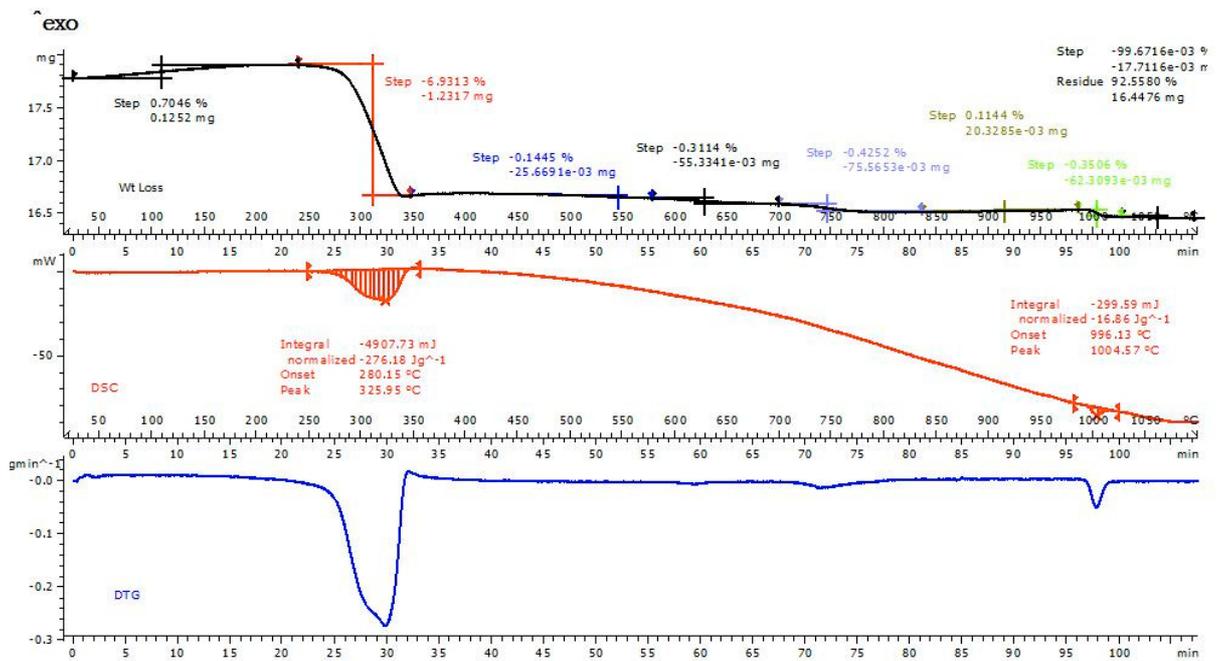
Figure 8.5 Mettler DSC-TG recorded on sample (4) Pr$_2$O$_3$ from 20°C to 1100°C under nitrogen.

The Mettler data shows the same deflection around 300°C. Additionally it identifies a deflection around 400°C (as figure 8.1) and 900°C (as figures 8.1 and 8.4). There is clearly a difference in the quality of the baseline between the machines. Of interest is the mass loss around 275°C, which has increased to 7.15% ie almost double that in figure 8.4. This indicates that the material is still absorbing gas from the atmosphere, the Mettler Toledo being used a month after the results from the Netzsch machine.

8.2 FULL RANGE DSC-TG IN AIR

Because of the possibility of sample (4) degrading further a new sample (6) Pr$_2$O$_3$ was obtained. The following image shows the initial DSC-TG recorded on this material.
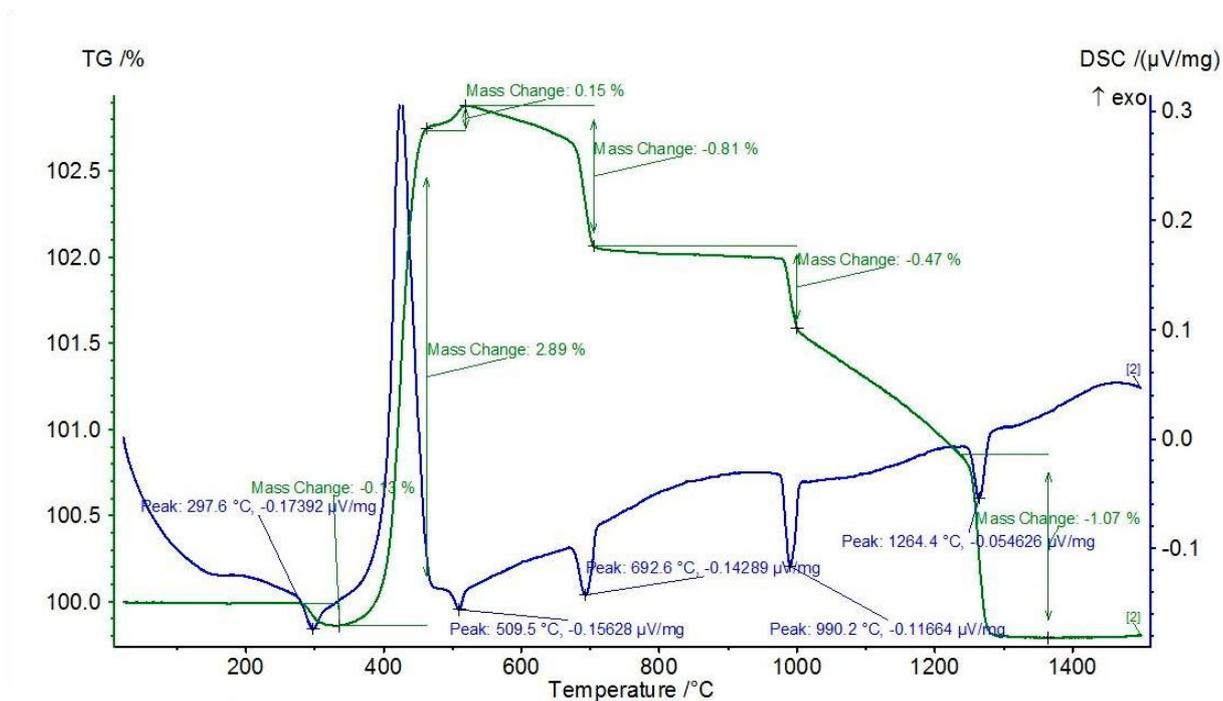
Fig 8.6 DSC-TG recorded on sample (6) from 20°C to 1500°C at 10K/min under air.

The DSC-TG for sample (6) was very different to those obtained from sample (4). Where, for sample (4), there had been a series of peaks around 300°C, there was now a small endotherm followed by a large exotherm. It was initially taken that this small endotherm might correspond to gas loss. Each deflection across the DSC was discernible as a discrete peak and many of these peaks could be related to known transitions on the Pr-O phase diagram. What is notable is that the broad hump had disappeared. The different look of the image for sample (6) is due to two factors. Firstly, sample (4) contained a mixture of cubic and hexagonal phases whereas sample (6) contained only the hexagonal phase. Secondly, sample (4) has absorbed significant gas before any DSC-TG work was performed on it. The degradation in the sample can be seen by comparing figures 7.7 and 7.34.

It is known from the Pr-O phase diagram that the ambient Pr_2O_3 phase oxidises at 275°C. From the sesquioxide phase diagram it is unclear at exactly what temperature the cubic phase will convert although it appears to be in the region of 500°C. Furthermore, the sesquioxide diagram does not show oxidation, although it should be assumed that heating cubic Pr_2O_3 is likely to result in oxidation too, presumably to Pr_6O_{11}. It may be that in addition to the sharp DSC peaks when the starting point is

pure hexagonal Pr_2O_3 there is some additional contribution from the cubic phase that masks the detail obtained from the pure hexagonal phase. Conversion of the cubic phase may be sluggish, occurring over much of the run, resulting in a wide hump, as shown in figures 8.1 to 8.4.

The TG for sample (6) shows a small mass loss of 0.13% around 275°C. This is likely to be gas loss from the sample; there has already been a small absorption from the air in the time the bottle had been opened. Following this mass loss there is a large gain of 2.89%, presumably due to oxidation. The expected mass gain for $Pr_2O_3 \rightarrow Pr_6O_{11}$ would be 3.2%.

8.3 RAMPS IN NITROGEN

The DSC data recorded during the 7 ramps performed on sample (4) are shown in figure 8.7 below.
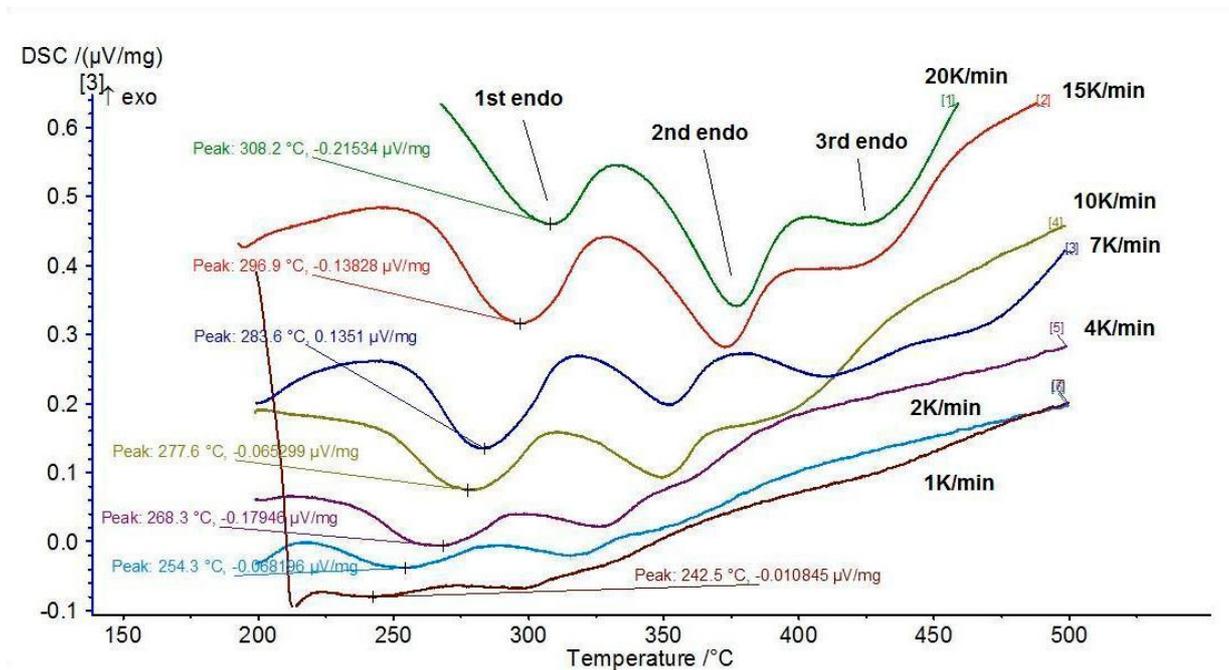
Figure 8.7 DSC recorded on sample (4) Pr_2O_3 from 200°C to 500°C under nitrogen.
Heating rates are indicated beside the lines.

The reaction appears to follow a three-stage process. This is understandable as there are likely to be deflections for the loss of gas, and also for both ambient phases converting

to the high-temperature phase. The table below lists the temperature ramps and the corresponding transition temperatures as identified by the maximum deflection for the first endotherm. The calculations are taken from the method given in Chapter 4.

Heating rate, ϕ (K/min)	Temp of max deflection, T_m (°C)	T_m (K)	T_m^{-1}	$Ln(\phi/T_m^2)$
1	242.5	515.7	0.001939	-12.491
2	254.3	527.5	0.001896	-11.843
4	268.3	541.5	0.001847	-11.202
7	277.6	550.8	0.001816	-10.677
10	283.6	556.8	0.001796	-10.342
15	296.9	570.1	0.001754	-9.984
20	308.2	581.4	0.001720	-9.735

Table 8.1 Kissinger analysis for 1st endotherm - sample (4) Pr_2O_3.

Figures 8.8 and 8.9 below show the plot of temperature against heating rate and the linear plot from which the activation energy can be calculated.
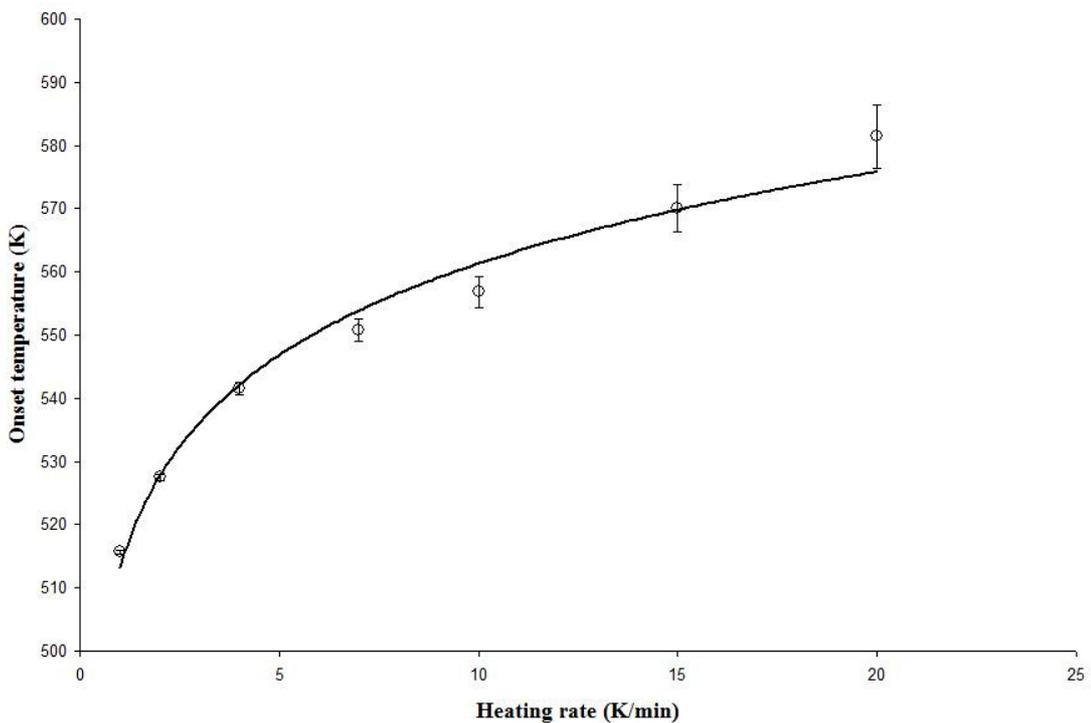
Figure 8.8 Temperature of maximum deflection, T_m, versus heating rate, ϕ, for sample (4) Pr_2O_3 1st endotherm.

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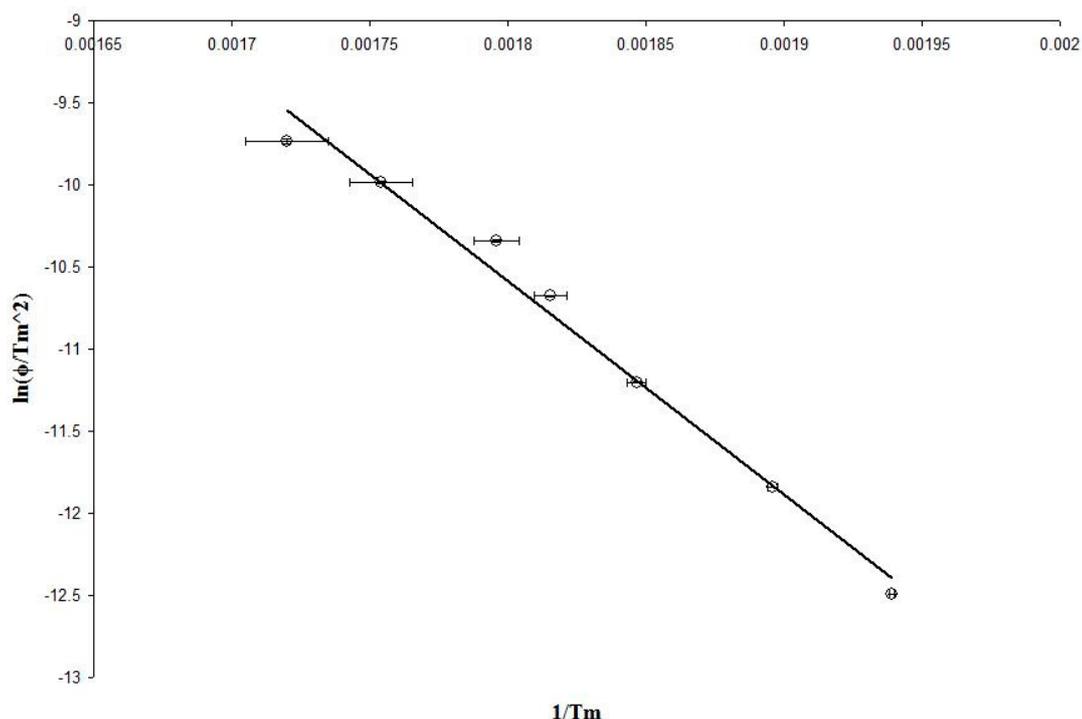
Figure 8.9 Plot of ln (ϕ /T_m^2) against $1/T_m$ for sample (4) Pr_2O_3 1st endotherm.

In chapter 4 it was shown that the gradient of the straight line is equal to $-E_A/R$. Therefore the activation energy was calculated to be 108(9) kJ.mol^{-1}.

Because the conversion is a multi-stage process (there are 3 endotherms) it was decided to analyse the other two peaks in the same way. Kissinger Analysis is dependent upon the shift in peaks with heating rate rather than their absolute positions, so this seemed a reasonable step to take.

ϕ (K/min)	T_m (°C)	T_m (K)	T_m^{-1}	ln(ϕ/T_m^2)
1	296.7	569.9	0.001755(4)	-12.691(6)
2	315.5	588.7	0.001699	-12.063(6)
4	326.6	599.8	0.001667	-11.407(6)
7	349.8	623	0.001605	-10.923(6)
10	351.8	625	0.001600	-10.573(6)
15	372.5	645.7	0.001549	-10.233(6)
20	377.0	650.2	0.001538	-9.959(6)

Table 8.2 Kissinger analysis for 2nd endotherm - sample (4) Pr_2O_3.
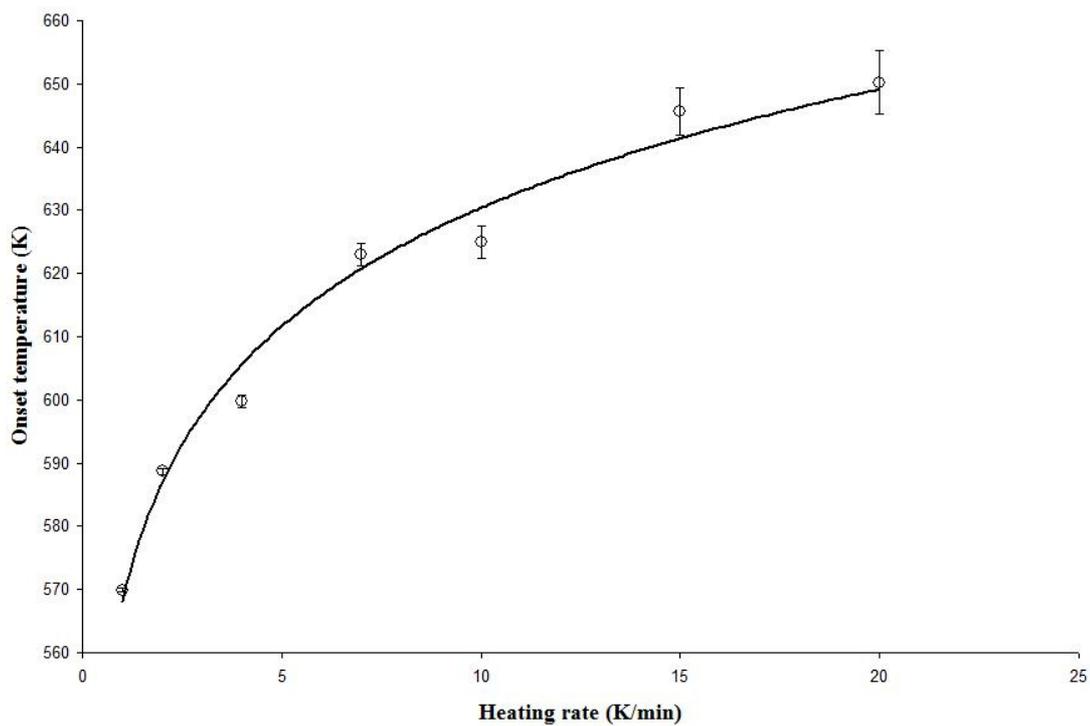
Figure 8.10 Temperature of maximum deflection, T_m, versus heating rate, ϕ, for sample (4) Pr_2O_3 2nd endotherm.

Figure 8.11 Plot of ln (ϕ /T_m^2) against 1/T_m for sample (4) Pr_2O_3 2nd endotherm.

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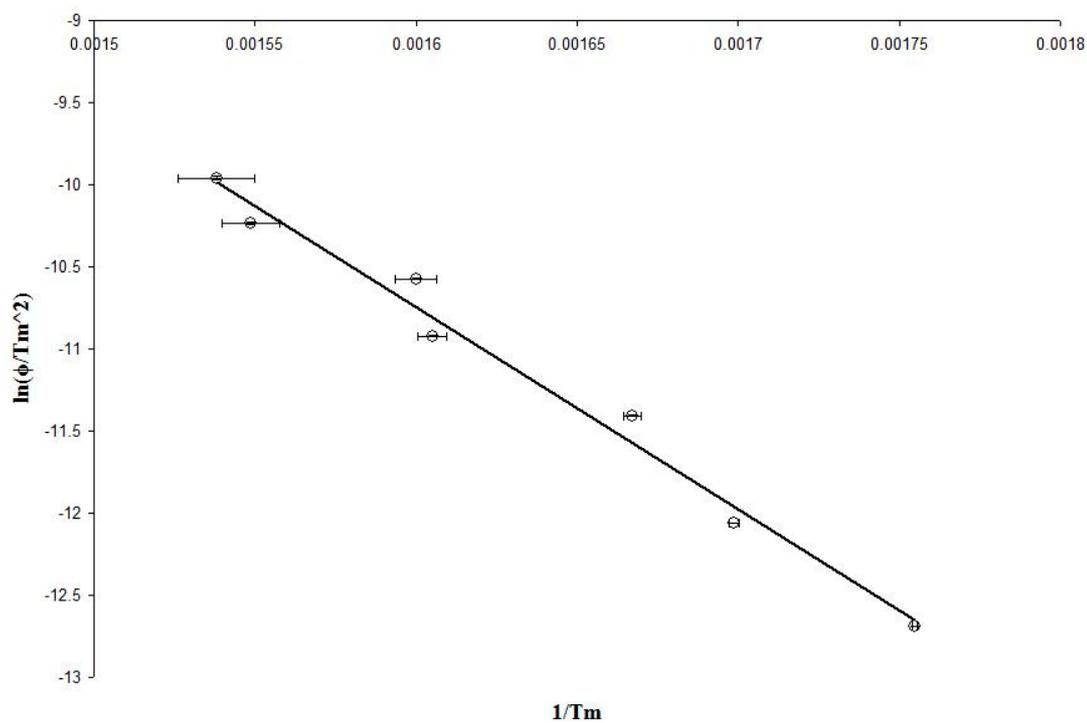
ϕ (K/min)	T_m (°C)	T_m (K)	T_m^{-1}	$\ln(\phi/T_m^2)$
1	Not discernible			
2	349.0	622.2	0.001607	-12.173(6)
4	361.0 (unclear)	634.2	0.001577	-11.518(6)
7	395.6 (unclear)	668.8	0.001495	-11.065(6)
10	410.3	683.5	0.001463	-10.752(6)
15	416.7 (unclear)	689.9	0.001449	-10.365(6)
20	422.9	696.1	0.001437	-10.095(6)

Table 8.3 Kissinger analysis for 3rd endotherm - sample (4) Pr_2O_3.
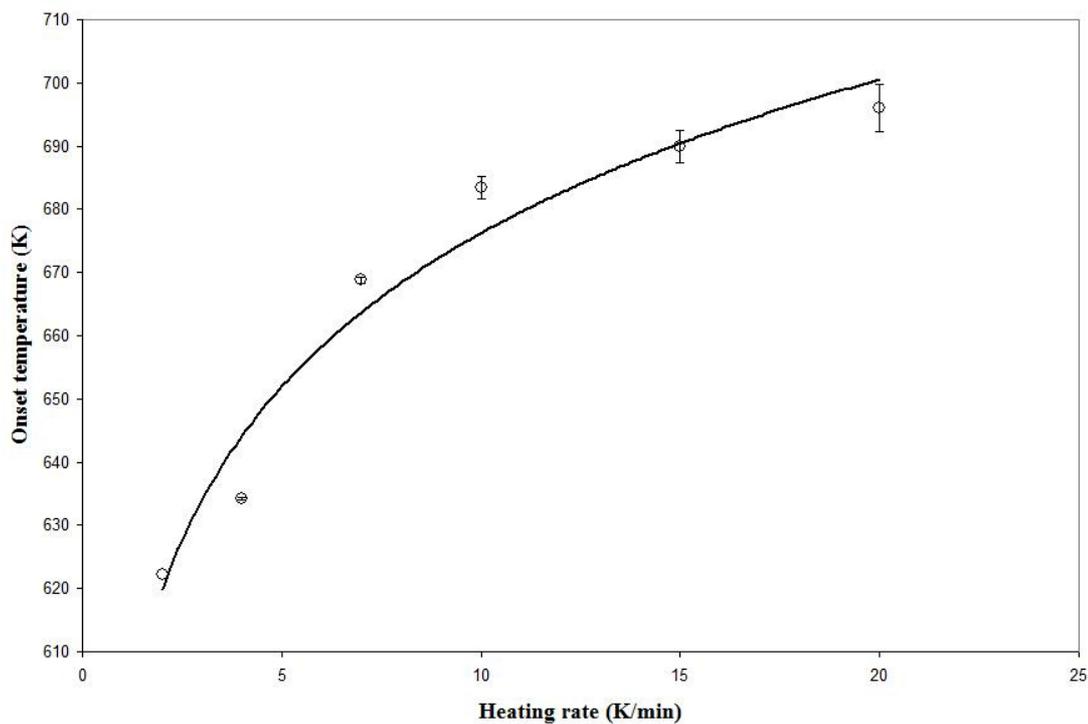
Figure 8.12 Temperature of maximum deflection, T_m, versus heating rate, ϕ, for sample (4) Pr_2O_3 3rd endotherm.
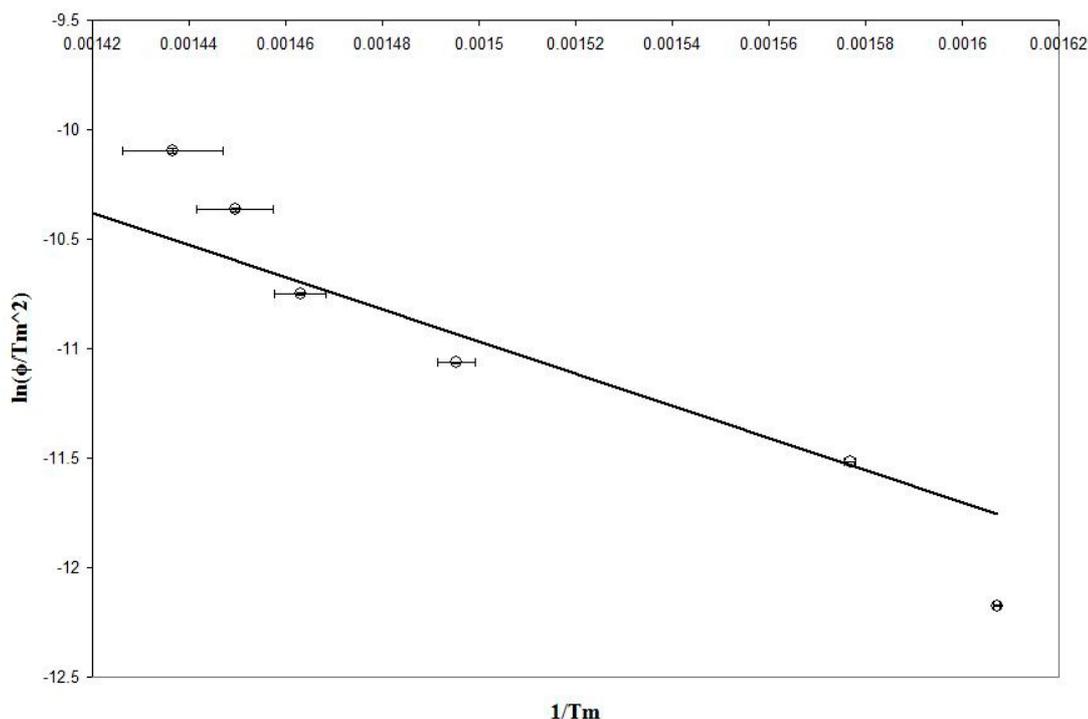
Figure 8.13 Plot of ln (ϕ /T_m^2) against 1/T_m for sample (4) Pr_2O_3 3rd endotherm.

The activation energy for endotherm 2 was calculated to be 103(6) kJ.mol^{-1} For endotherm 3 the figure is 61(3) kJ.mol^{-}1 if all data points are used. However, there was some difficulty measuring the troughs for the 4, 7 and 15K/minute runs. The Netzsch software was unable to pick them up and so they had to be determined manually. Omitting these 3 points the figure is 56(3) kJ.mol^{-1}, which is still close to the former reading.

8.4 RAMPS IN AIR

8.4.1 Ramp performed between 20°C and 600°C

The DSC recorded during the 7 ramps performed between 20°C and 600°C on sample (6) are shown in figure 8.14 below.
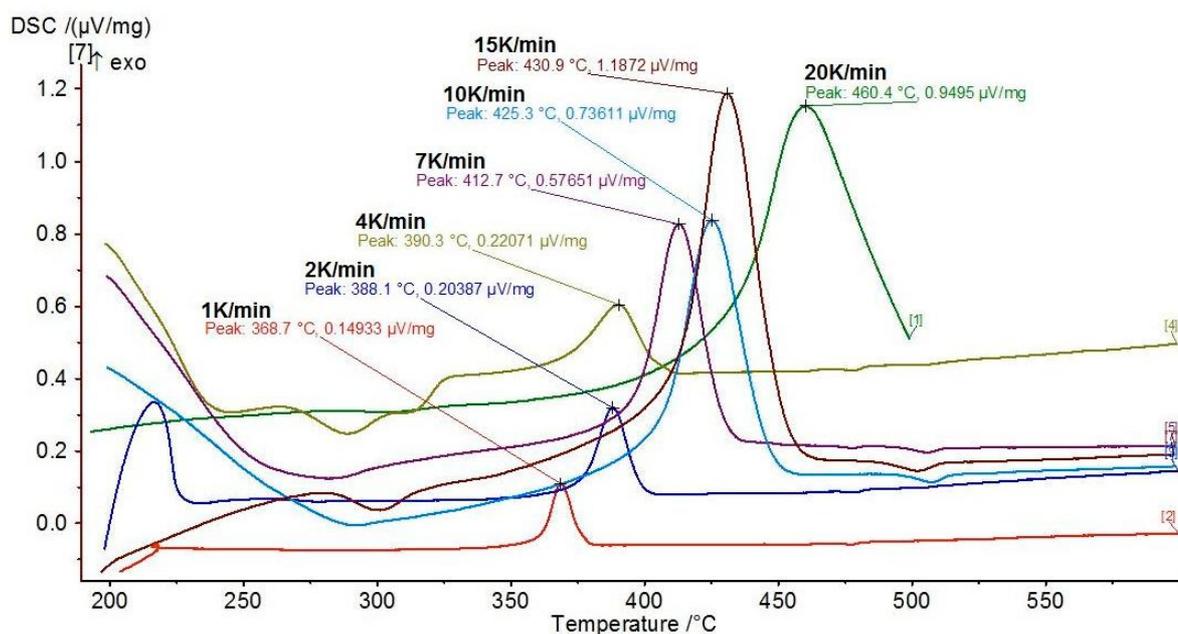
Figure 8.14 DSC ramps on sample (6) Pr_2O_3 from 200 °C to 600 °C in air.

As with figure 8.6, the DSC data collected from sample (6) shows a single deflection around 400°C rather than the three shown by sample (4). The sample (6) deflections do not follow as smooth a shift with heating rate as for sample (4); the 15K/min and 10K/min peaks are close, as are those for 4K/min and 2K/min. The table below lists the temperature ramps and the corresponding temperatures of the maximum deflection for this exotherm.

ϕ (K/min)	T_m (°C)	T_m (K)	T_m^{-1}	$\ln(\phi/T_m^2)$
1	368.7	641.9	0.001558	-12.929
2	388.1	661.3	0.001512	-12.295
4	390.3	663.5	0.001507	-11.609
7	412.7	685.9	0.001458	-11.116
10	425.3	698.5	0.001432	-10.795
15	430.9	704.1	0.001420	-10.406
20	460.4	733.6	0.001363	-10.200

Table 8.4 Kissinger analysis for 1st exotherm - sample (6) Pr_2O_3. Data recorded from 200 °C to 600 °C.

Figures 8.15 and 8.16 below show the plot of temperature against heating rate and the linear plot from which the activation energy can be calculated.

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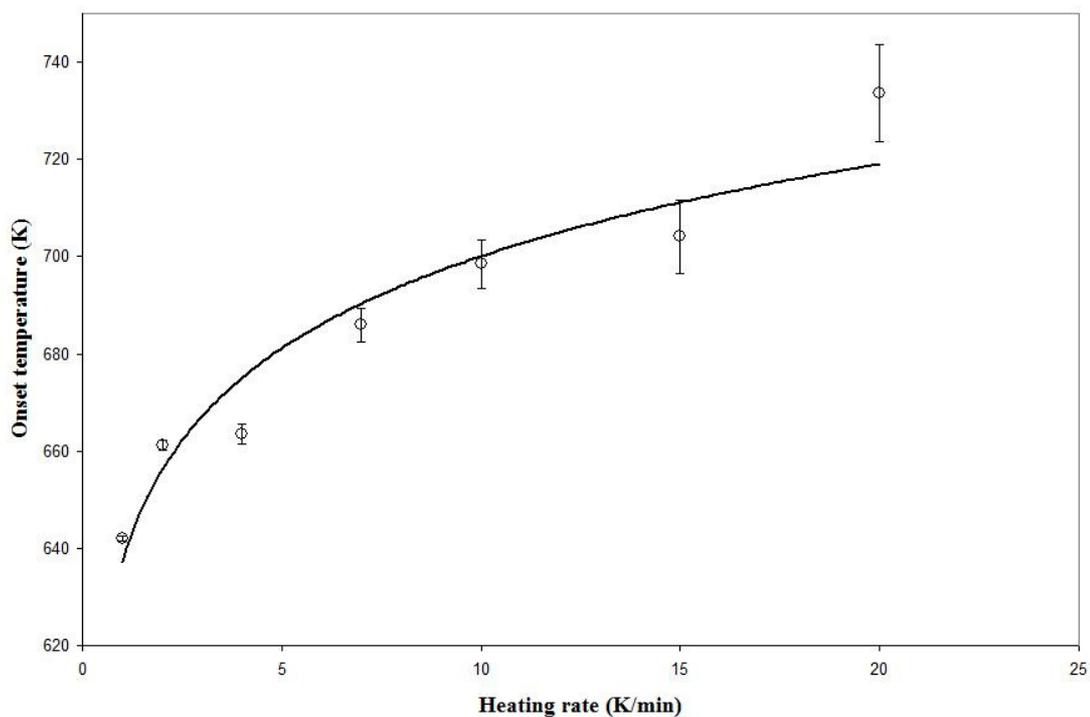
Figure 8.15 Temperature of maximum deflection, T_m, versus heating rate, ϕ, for sample (6) Pr_2O_3 1st exotherm.
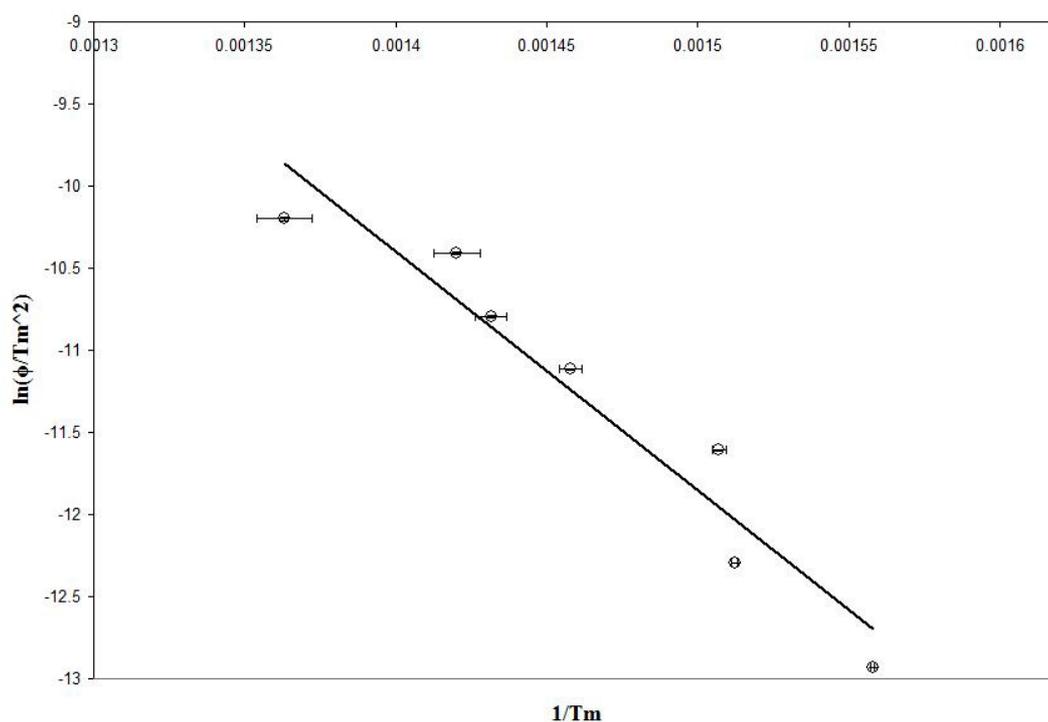
Figure 8.16 Plot of ln (ϕ /T_m^2) against 1/T_m, for sample (6) Pr_2O_3 1st exotherm.

The activation energy for the exotherm in sample (6) was calculated to be -122(6) kJ.mol^{-1}. It was notable that the DSC data for the 4K/min ramp showed other features,

similar to figure 8.7 and presumably due to gas absorption. This was confirmed by the associated TG plot, which was very different to those for the other ramps. Furthermore, the temperature of maximum deflection for the 4K/min ramp lies unusually close to that for the 2K/min ramp (see table 8.4), again presumably because of sample contamination. Omitting the 4K/min data point the activation energy becomes -128(6) kJ.mol^{-1}.

It is notable that figures 8.7 and 8.17 both show a smooth shift of peak position with heating rate. However, there still appears to be a problem with figure 8.14 in that the 20K/min data point does not follow this trend. The exact reason for this is not known and due to instrument availability it was not possible to repeat the recording. Although it would have been useful to repeat the 20K/min ramp, if both 20K/min and 4K/min data points are omitted the value for the activation energy is -152(8) kJ.mol^{-1}.

8.4.2 Ramp performed between 20°C and 1500°C

The DSC recorded for the 7 ramps performed between 20°C and 1500°C on sample (6) are shown in figure 8.17 below. The labelled peak is the 1st exotherm.
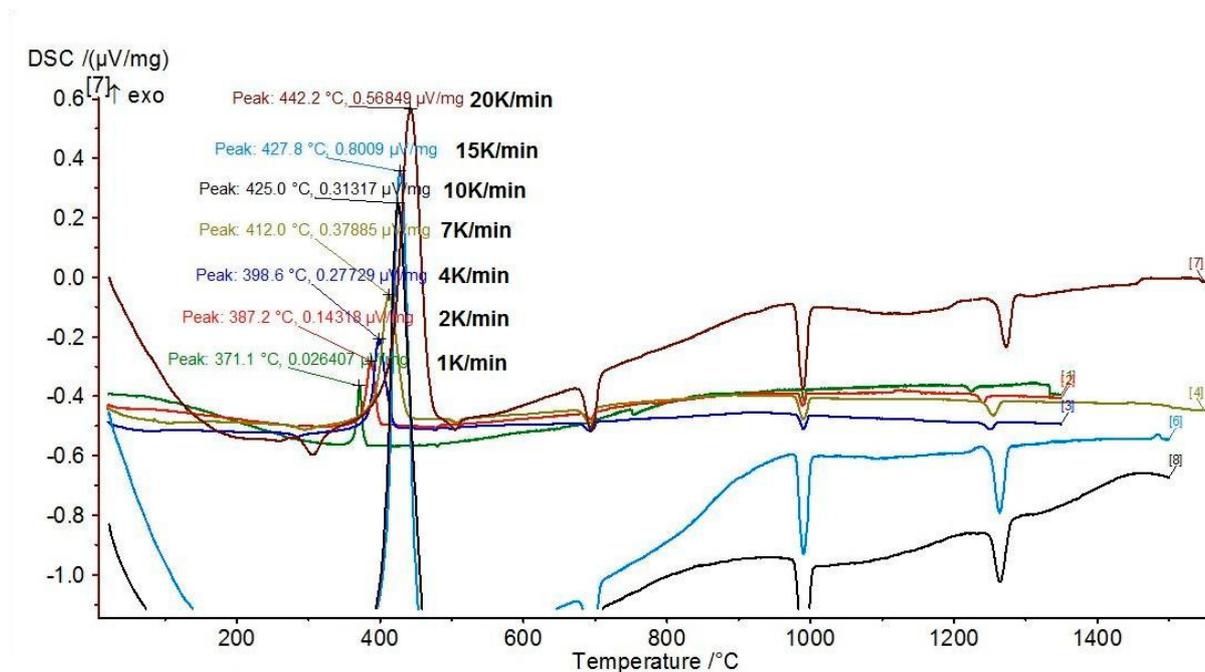
Figure 8.17 DSC ramps on sample (6) Pr$_2$O$_3$ from 20°C to 1500°C in air.

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The change in peak temperature with heating rate is more uniform than for the 20°C to 600°C run, although the 15K/min and 10K/min peaks are still close. The table below lists the temperature ramps and the corresponding temperatures of the maximum deflection for the same exotherm studied in the 20°C to 500°C runs above.

ϕ (K/min)	T_m (°C)	T_m (K)	T_m^{-1}	$\ln(\phi/T_m^2)$
1	371.1	644.3	0.001552	-12.936
2	387.2	660.4	0.001514	-12.292
4	398.6	671.8	0.001489	-11.634
7	412	685.2	0.001460	-11.113
10	425	698.2	0.001432	-10.794
15	427.8	701.0	0.001427	-10.397
20	442.2	715.4	0.001398	-10.150

Table 8.5 Kissinger analysis for 1st exotherm - sample (6) Pr$_2$O$_3$. Data recorded from 20°C to 1500°C.

Figures 8.18 and 8.19 below show the plot of temperature against heating rate and the linear plot from which the activation energy can be calculated.
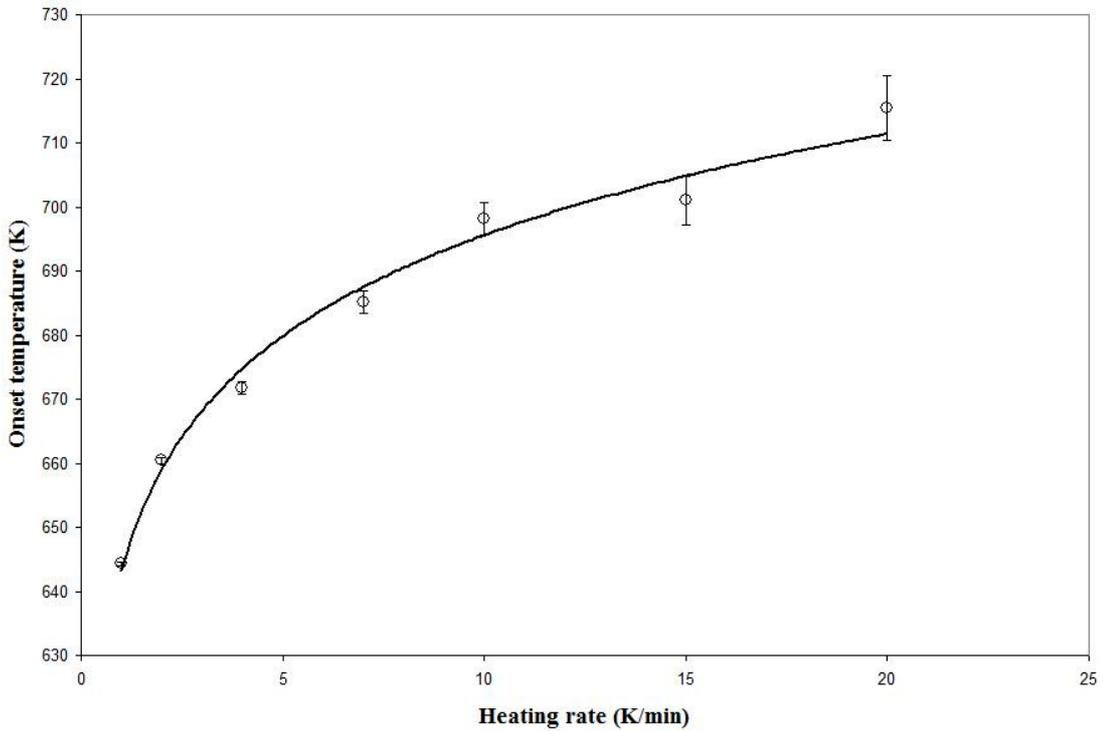
Figure 8.18 Temperature of maximum deflection, T_m, versus heating rate, ϕ, for sample (6) Pr$_2$O$_3$ 1st exotherm.
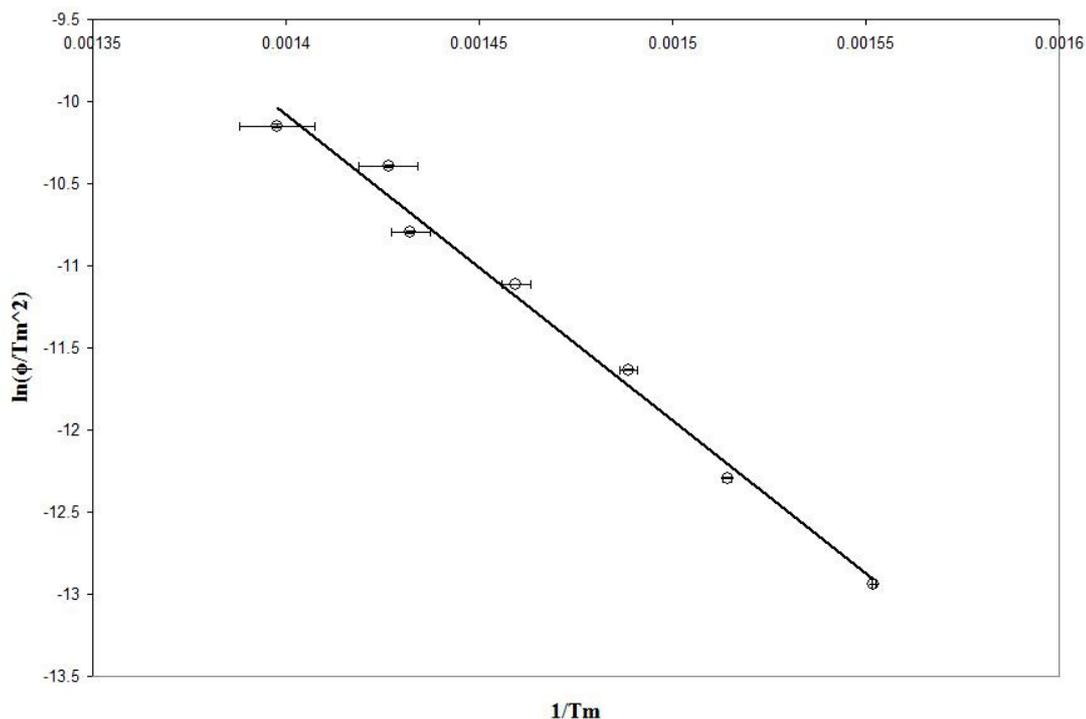
Figure 8.19 Plot of ln (ϕ /$T_m{}^2$) against 1/T_m for sample (6) Pr_2O_3 1st exotherm.

Analysis of the above results gave an activation energy for the exotherm in sample (6) of -155(10) kJ.mol^{-1}.

The data in figure 8.17 was also used to examine the four deflections above 400°C. The only transition which produced meaningful data was the one occurring around 1250°C, where the σ phase converts to the highest temperature phase of θ Pr_2O_3. The data for this endotherm is given in table 8.6 below.

ϕ (K/min)	T_m (°C)	T_m (K)	$T_m{}^{-1}$	ln(ϕ/$T_m{}^2$)
1	1224.3	1497.5	0.0006680	-14.622
2	1240.2	1513.4	0.0006609	-13.951
4	1250.3	1523.5	0.0006566	-13.271
7	1254.9	1528.1	0.0006545	-12.716
10	1264.4	1537.6	0.0006506	-12.373
15	1263.9	1537.1	0.0006510	-11.966
20	1273.1	1546.3	0.0006468	-11.691

Table 8.6 Kissinger analysis for endotherm at 1250°C - sample (6) Pr_2O_3. Data recorded from 20°C to 1500°C.

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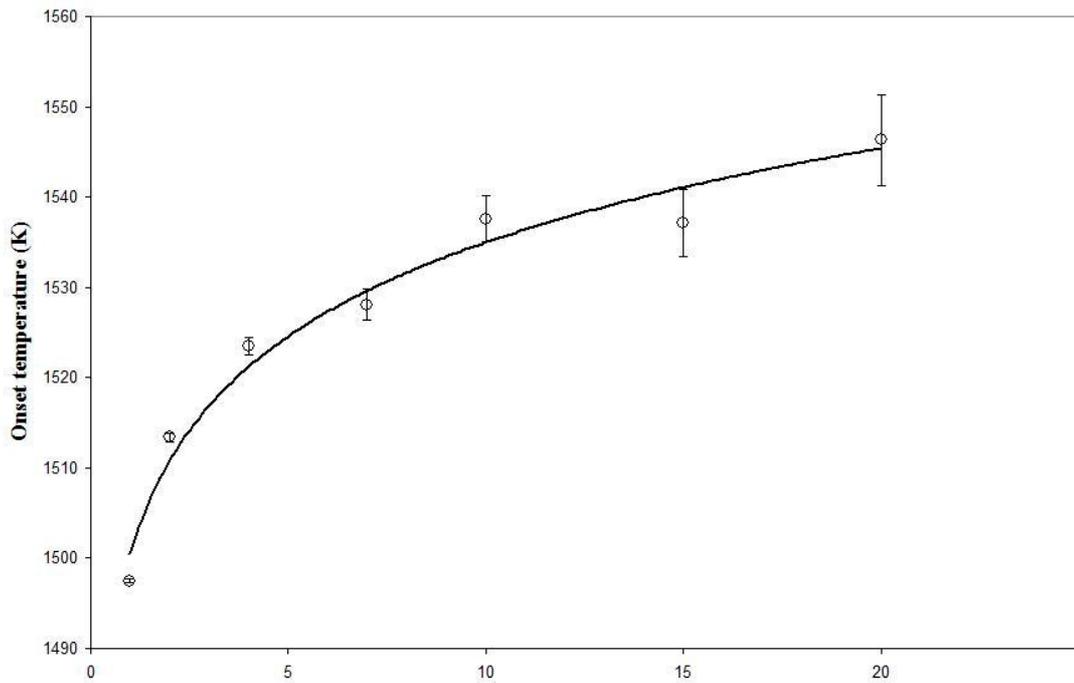
Figure 8.20 Temperature of maximum deflection, T_m, versus heating rate, ϕ, for sample (6) 1250°C endotherm.
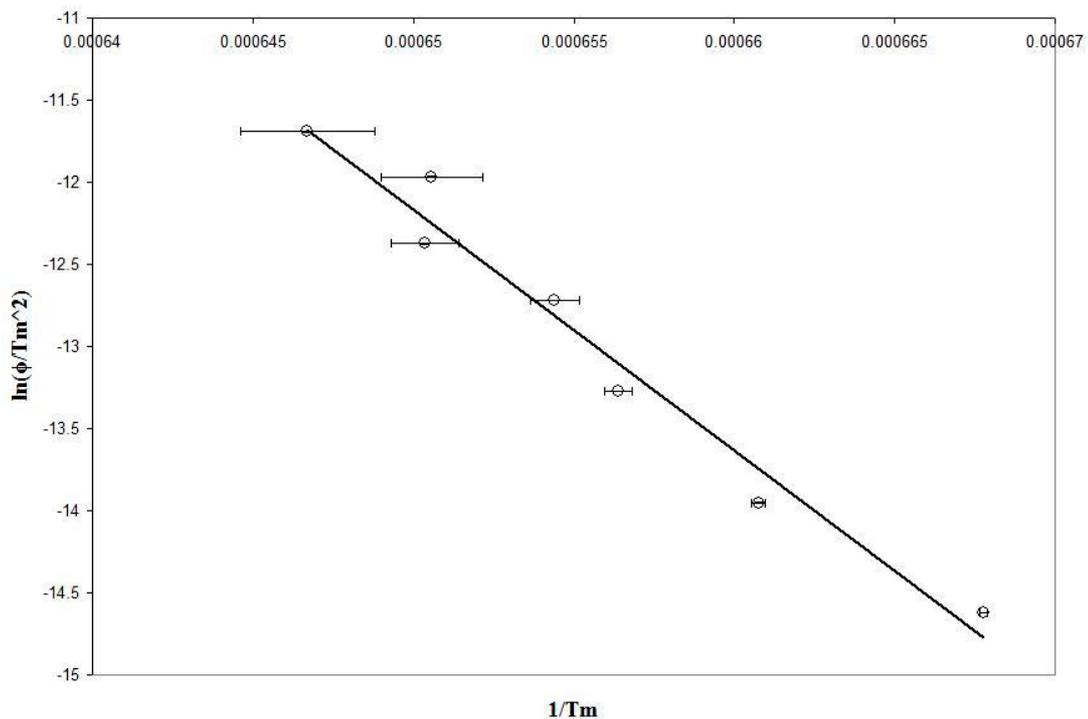
Figure 8.21 Plot of ln (ϕ /T_m^{2}) against $1/T_m$, for sample (6) 1250°C endotherm.

Analysis of the above results gave an activation energy of 1224(122) kJ.mol^{-1} for the endotherm at 1250°C.

8.4.3 Summary of activation energies

Sample	Ramp	Peak	EA_1 (kJ.mol^{-1})	EA_2*	EA_3*
(4) Pr_2O_3	200°C to 500°C	1st endotherm	108(9)		
(4) Pr_2O_3	200°C to 500°C	2nd endotherm	103(6)		
(4) Pr_2O_3	200°C to 500°C	3rd endotherm	61(3)		
(6) Pr_2O_3	20°C to 500°C	1st exotherm	-122(6)	-128(6)	-152(8)
(6) Pr_2O_3	20°C to 1500°C	1st exotherm	-155(10)		
(6) Pr_2O_3	20°C to 1500°C	1250°C endotherm	1224(122)		

*Table 8.7 Activation energies for phase changes in samples (4) and (6). * indicates omitted data point(s).*

8.5 TWO-DIRECTIONAL DSC-TG: 20°C TO 1400°C AND BACK

To determine whether any of the transitions in the Pr-O system were reversible, sample (6) was heated to 1400°C and cooled back again. The recorded DSC is shown in figure 8.22.
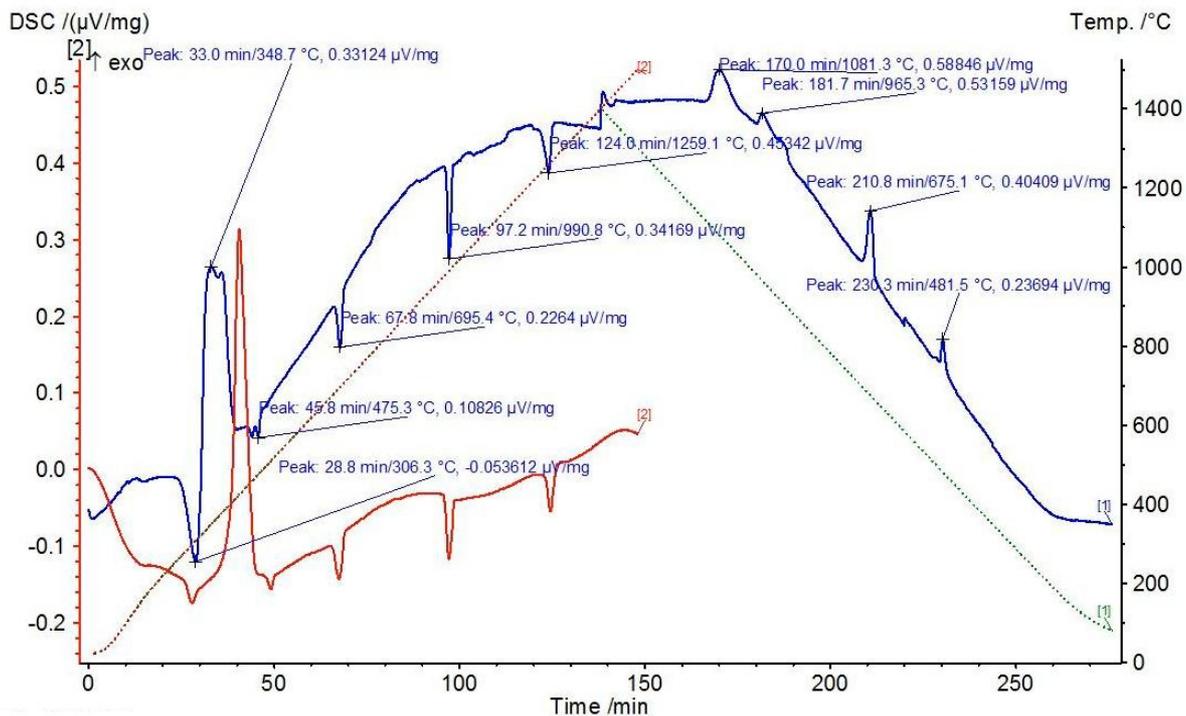
Figure 8.22 DSC recorded on sample (6) Pr₂O₃ from 20°C to 1400°C and back at 10K/min in air. The data collected from 20°C to 1500°C (from figure 8.6) is shown on the left for comparison.

There is a clear vertical correlation in figure 8.22 between the two lines, as should be expected since they are of the same sample, albeit at different ages. As this was one of the later experiments on sample (6) there has been considerable gas absorption, shown by the TG curve in figure 8.23, below.
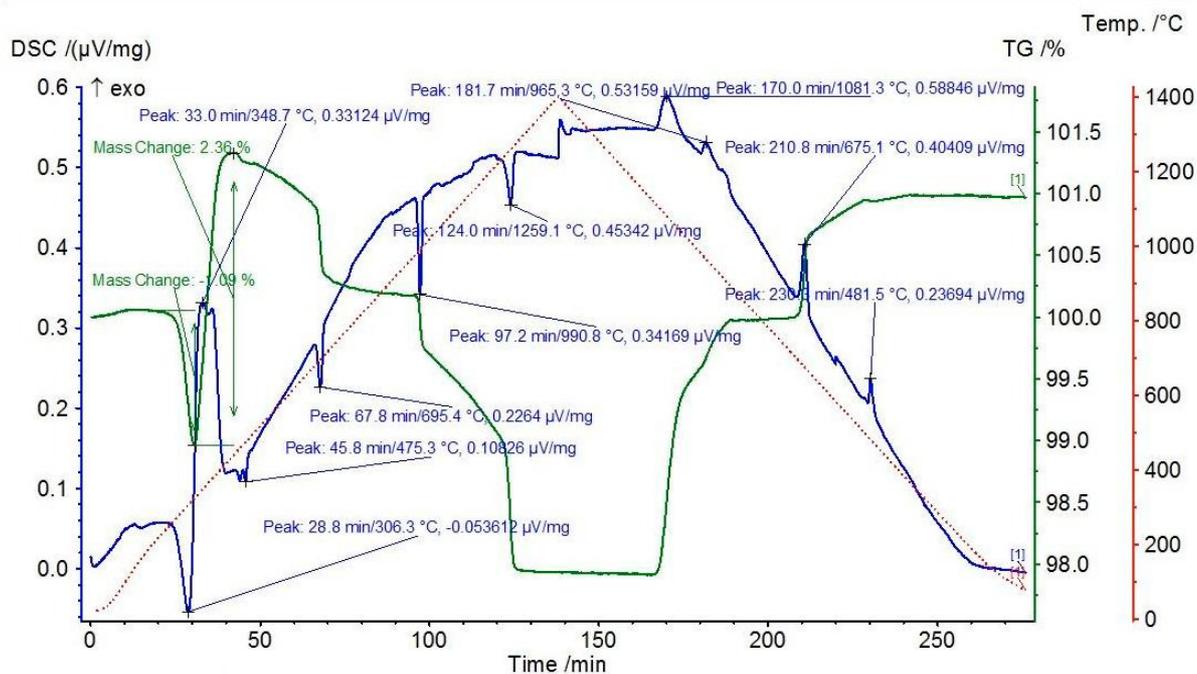
Figure 8.23 DSC-TG recorded on sample (6) Pr₂O₃ from 20°C to 1400°C and back at 10K/min in air.

Figure 8.6 showed a mass loss on sample (6) of 0.13% and a mass gain due to oxidation of 2.89%. Figure 8.23 shows the sample 2 months later. There is now a greater mass loss (1.09%). There is also a change to the profile of the corresponding exotherm for the oxidation. Other than the weight loss at approximately 300°C, the TG appears fairly symmetrical about the centre of the figure. This point represents 1400°C where the instrument began to cool the sample. Figure 8.24 shows a wrapped image.
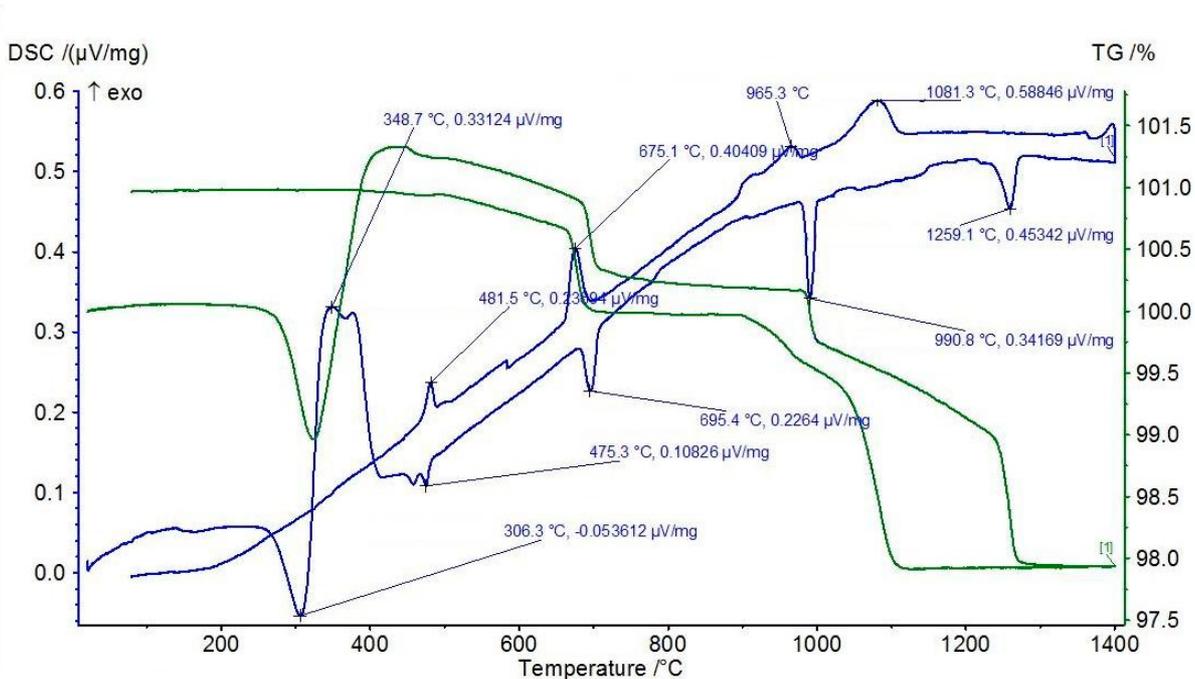
Figure 8.24 DSC-TG recorded on sample (6) Pr₂O₃ from 20 °C to 1400 °C and back at 10K/min in air. Image wrapped to compare associated transitions.

Figure 8.25 shows the values for the mass changes.
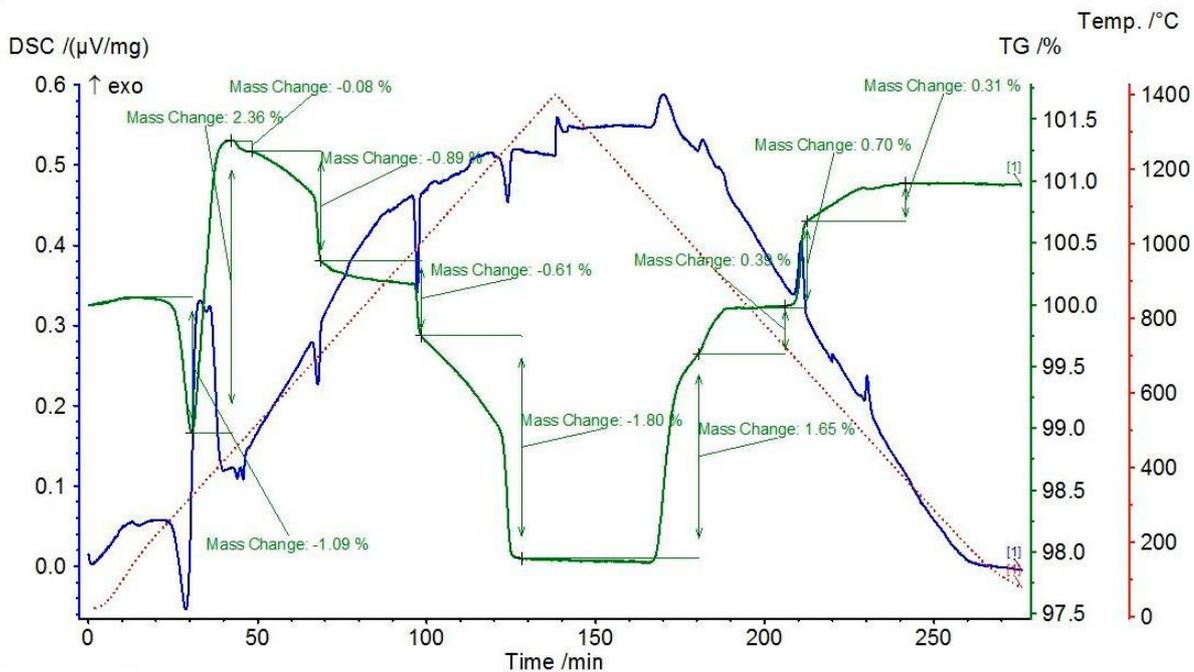
Figure 8.25 DSC-TG recorded on sample (6) Pr₂O₃ from 20 °C to 1400 °C and back at 10K/min in air. Mass changes are shown.

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The transition temperatures and mass changes occurring during the heating and cooling ramp show hysteresis. This has been tabulated below.

Feature	DSC temp (°C)	TG temp (°C)	Mass change (%)	Ramp
1	306.3	264.8	-1.09	Heating
2	348.7	322.3	+2.36	Heating
3^1	475.3	452.7	-0.09	Heating
4^2	695.4	688.0	-0.88	Heating
5^3	990.8	981.5	-0.61	Heating
6^4	1259.1	1238.1	-1.80	Heating
7^4	1081.3	1114.4	+1.65	Cooling
8^3	965.3	970.8	+0.39	Cooling
9^2	675.1	697.0	+0.70	Cooling
10^1	481.5	493.4	+0.31	Cooling

Table 8.8 Transition temperatures for sample (6) Pr_2O_3 taken from 10K/min DSC-TG data. Paired transitions are indicated by superscripts.

Figure 8.25 and table 88 indicate that the final state of the material is the β phase, Pr_6O_{11}. For each DSC deflection and mass change when the temperature is rising, other than the initial gas loss and the first oxidation to Pr_6O_{11}, there is a corresponding reversal when the temperature is falling. The β phase is therefore stable under ambient conditions, also demonstrated by the pan containing a red-black powder rather than the green of the sesquioxide.

8.6 GAS ABSORPTION

Praseodymium sesquioxide is known for absorbing both water and carbon dioxide readily from the air. As discussed earlier in this chapter, if gas was being lost at the point of phase change, this relatively large mass loss would hide the small gain due to oxidation. The image below shows the DSC-TG on sample (6) taken after 85 days from opening the sample. A portion of sample (6) was spread in a thin layer and left directly exposed to the air. The weight loss results for this experiment on sample (6) are given below in table 8.9.
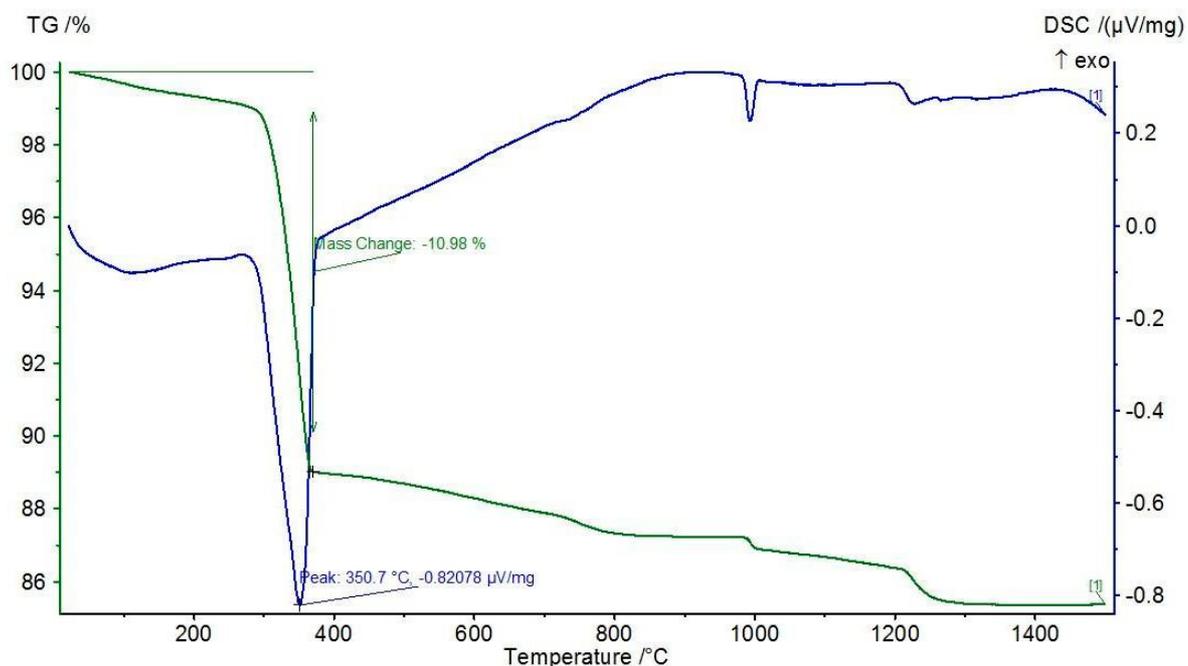
Fig 8.26. Gas loss from sample (6) Pr$_2$O$_3$ after 85 days' exposure to air.

It is interesting to note the change in the DSC-TG from that shown in figure 8.6. The large exotherm at around 400°C in figure 8.6 has gone, replaced by a large endotherm. This endotherm appears to be the same as the 1st endotherm in the DSC-TG for sample (4). As it was known that sample (6) was a pure hexagonal phase, it can be proposed that this point corresponds to release of bound gas from the material, there being no endo/exotherms associated with a structural change from the ambient cubic phase. The same endotherm exists in DSC-TG runs for earlier runs of sample (6), when there was much less gas contamination; figure 8.6 shows a small endotherm at 297.6°C, before the large exotherm at 425°C which represents the phase change. Other than this, the remaining deflections in both the DSC and TG appear to match up, indicating that the material present above 425°C is the same.

Time (days)	Weight loss (%)	Temperature of endotherm (°C)
7 (1st measurement)	-10.50	370.0
7 (2nd measurement)	-10.33	372.0
78	-11.30	347.1
85	-11.14	350.7

Table 8.9 Weight loss on sample (6) Pr$_2$O$_3$ on exposing to air.

Assuming that it is water that is being absorbed, the following calculations can be made:

Original material (Pr_2O_3) + water → hydrates to the hydroxide $Pr(OH)_3$

RMM of Pr_2O_3 (equivalent to $PrO_{1.5}$) is 329.8 (164.9 per Pr atom)

RMM of $Pr(OH)_3$ is 191.924

RMM of Pr_6O_{11} (equivalent to $PrO_{1.833}$) (the β phase of praseodymium oxide) is 1021.4 (170.23 per Pr atom)

Assuming the reaction proceeds as follows:

	loss of water		oxidation	
$Pr(OH)_3$	→	**$PrO_{1.5}$**	→	**$PrO_{1.833}$**
RMM 191.124		RMM 164.9*		RMM 170.23*
		-13.7%		**+3.23%**

* equivalent mass relative to one atom of Pr

This loss of water followed by oxidation should therefore result in a net mass change of –10.9%. This is very close to the figure of –11.14% measured after 85 days of exposing powdered sample (6) to the atmosphere, which indicates that it is indeed hydrating to the hydroxide. It should be noted that prior to the DSC-TG work the sample bottle had been in use for 4 months, albeit closed for much of the time, and so some degradation would also have occurred during this period. Table 8.8 only shows further degradation when it was decided to completely expose the sample to the air. Sample (6) arrived as sintered chips rather than powder; it is believed that this afforded it some protection from the air, due to the reduced surface area exposed to the atmosphere. As a comparison, sample (4) had already degraded within the bottle prior to the DSC being used.

8.7 RELATING THE DSC-TG TO THE PHASE DIAGRAM

As already discussed, the Pr-O phase diagram is complex and this is reflected in the DSC-TG for sample (6). Figure 8.6 shows that after the gas loss endotherm, there are 5 deflections in the DSC. Figure 8.27 below shows all the peaks and mass changes with labels.
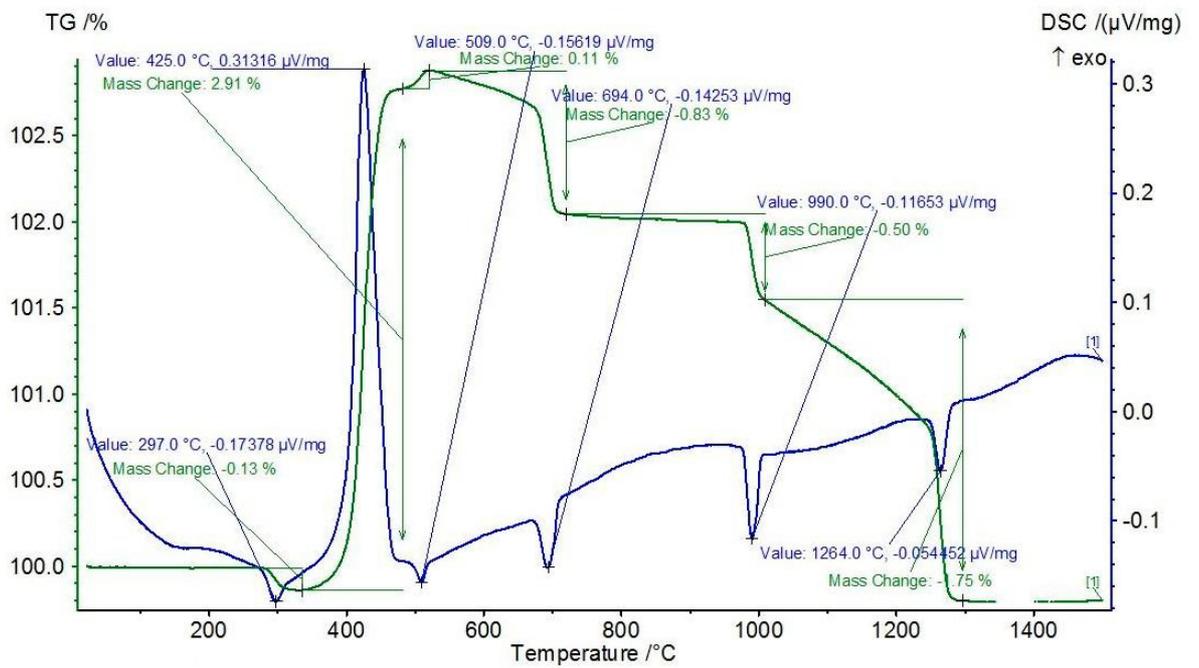
Fig 8.27 DSC-TG recorded on sample (6) Pr$_2$O$_3$ from 20°C to 1500°C at 10K/min in air. Mass changes are indicated.

Because of the additional weight due to water absorption, the TG values need to be adjusted such that the mass is 100% after the first weight loss. Figure 8.25 below is a plot of temperature versus x in PrO$_x$ following this adjustment for the 10K/minute ramp. The inset shows the known phases. The points labelled 1 to 7 identify the phases of interest.
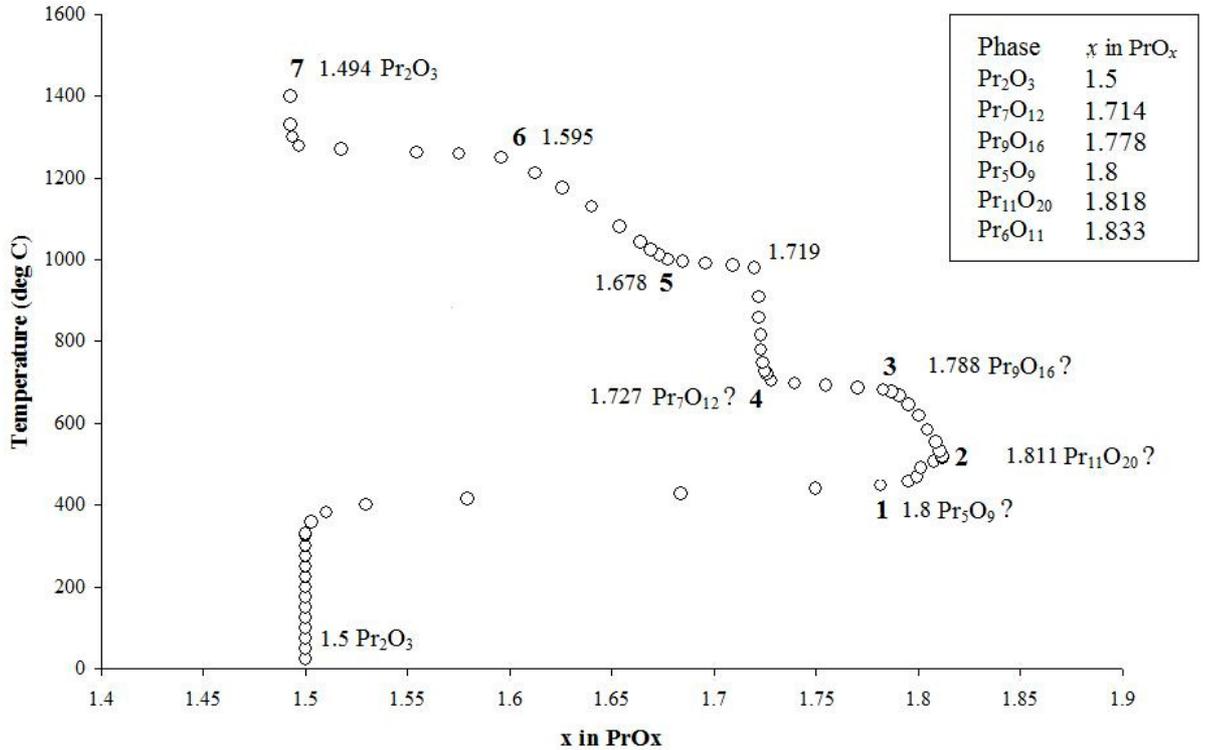
Figure 8.28 Temperature versus oxygen in the Pr-O system for DSC recorded on sample (6) Pr$_2$O$_3$ at 10K/min in air.

Figure 8.28 shows that the ambient form of hexagonal Pr$_2$O$_3$ is stable up to about 350°C where there is a sudden and significant mass gain to point 1 (PrO$_{1.800}$), followed by a small and gradual mass gain to poin 2 (PrO$_{1.811}$) and a small and gradual mass loss to point 3 (PrO$_{1.788}$). These three points clearly correspond to the area of the phase diagram where the β, δ, ε and ζ phases lie. However, to ascertain exactly which phase corresponds to which point in figure 8.28 is difficult, particularly because the stoichiometries of these phases are very close. The phase with highest oxygen content is expected to be Pr$_6$O$_{11}$ (PrO$_{1.833}$). However, the highest value of x from the 10K/min run was 1.811, implying this phase was actually Pr$_{11}$O$_{20}$. The gradual mass loss from x = 1.811 to 1.788 does not indicate any of the discrete phases (the closest would be the ζ phase) but instead the non-stoichiometric α phase, the boundary for which, in figure 1.9, follows a similar slope. From x = 1.788 there is a sudden drop to 1.727 at about 700°C. This appears to mark the appearance of the ι phase of Pr$_7$O$_{12}$. As in the phase diagram the stoichiometry is steady up to about 1000°C, where there is a sudden drop to x = 1.678. This phase gradually loses oxygen for the next 250 degrees and represents

a wide range of oxygen content, down to $x = 1.595$. Finally, at about 1250°C there is a sudden mass loss to the θ phase of Pr_2O_3. Figure 8.29 shows the combined TG data from all runs on sample (6) and table 8.10 gives the values of x in PrO_x.
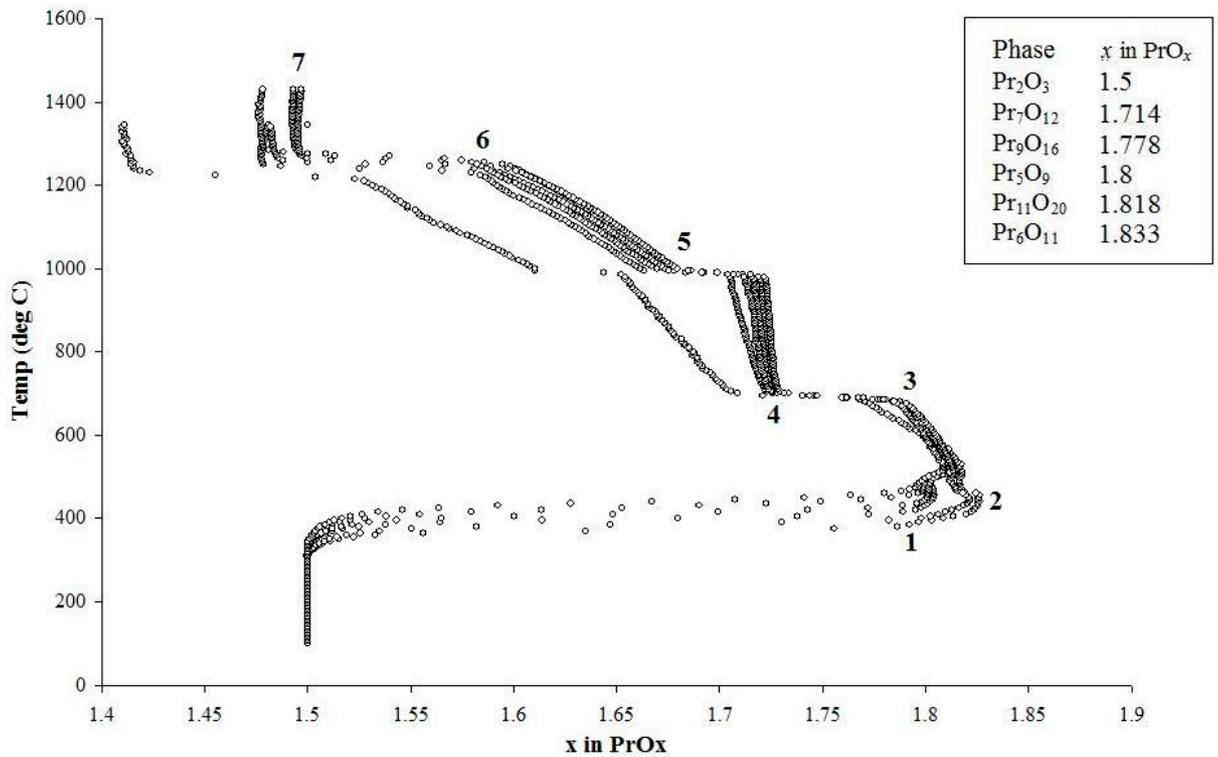
Figure 8.29 Temperature versus oygen content for all DSC recorded on sample (6) Pr_2O_3 from 20 ℃ to 1500 ℃ in air. Labels correspond to superscipt numbers in table 8.10.

Ramp	375°C[1]	530°C[2]	680°C[3]	705°C[4]	1000-1250°C[5-6]	1275°C[7]
1K/min	1.786	1.827, 1.817, 1.818	1.768	1.709	1.611 to 1.523	1.411
2K/min	1.798	1.822, 1.816, 1.812, 1.814	1.781	1.726	1.664 to 1.580	1.481
4K/min	1.789	1.804, 1.802, 1.812	1.785	1.728	1.678 to 1.590	1.482
7K/min	1.789	1.801, 1.802, 1.813	1.788	1.732	1.680 to 1.598	1.497
10K/min	1.792	1.800, 1.801, 1.811	1.788	1.728	1.678 to 1.595	1.493
20K/min	1.788	1.795, 1.800, 1.809	1.785	1.725	1.670 to 1.580	1.478

Table 8.10 Values of x in PrO_x for DSC-TG recorded on sample (6). Superscripts beside temperatures correspond to points in figures 8.28 and 8.29.

All but one of the runs in figure 8.26 show precision; however, the run at 1K/min has deviated somewhat, shown particularly by the final value of x being 1.411. The 1K/min and 2K/min runs both show an intial maximum in the TG, followed by a small

decrease, a small increase, then a fall; the other runs build to the maximum. The exact route through the phases in this temperature region therefore appears different depending upon the heating rate. The largest of these maxima is shown by the 1K/min run at an oxygen content of 1.827. As the 2 highest values for x on the phase diagram are 1.818 and 1.833, it is reasonable to assume that this maximum point corresponds to the β phase of Pr_6O_{11}. It is notable that amongst the remaining ramps the maximum oxygen content was only 1.811, implying the presence of the δ phase $Pr_{11}O_{20}$, the β phase Pr_6O_{11} not being attained.. With the deviation in the 1K/min final value, it might be expected that all the 1K/min values were unreliable. However, the 1K/min and 2K/min ramps shows a proximity in their values for the oxygen contents across the majority of the temperature range. The 2K/min ramp maximum of 1.822 correlates with the maximum for the 1K/min ramp, indicating that the β phase is indeed present.

The first mass change gives a value of x of approximately 1.790, which appears to be the ε phase. The order of the phases as they appear for the 1K/min and 2K/min ramps is therefore believed to be as in table 8.11. For the remaining ramps the only difference appears to be that the δ phase appears immediately before the β phase.

Phase	Temperature (°C)	x in PrO_x (from TG)	Formula
ε	400-420	1.798-1.813	Pr_5O_9
β	420-445	1.813-1.822	Pr_6O_{11}
δ	470-490	1.815-1.812	$Pr_{11}O_{20}$
α	520-680	1.814-1.785	Non-stoichiometric
ι	705-985	1.723-1.704	Pr_7O_{12}
σ	995 to 1225	1.664-1.584	Non-stoichiometric
θ	1250-	1.479-1.481	Pr_2O_3

Table 8.11 Order of appearance of phases in the Pr-O system with temperature for the 2K/min ramp.

This information is also shown in figure 8.30, below.
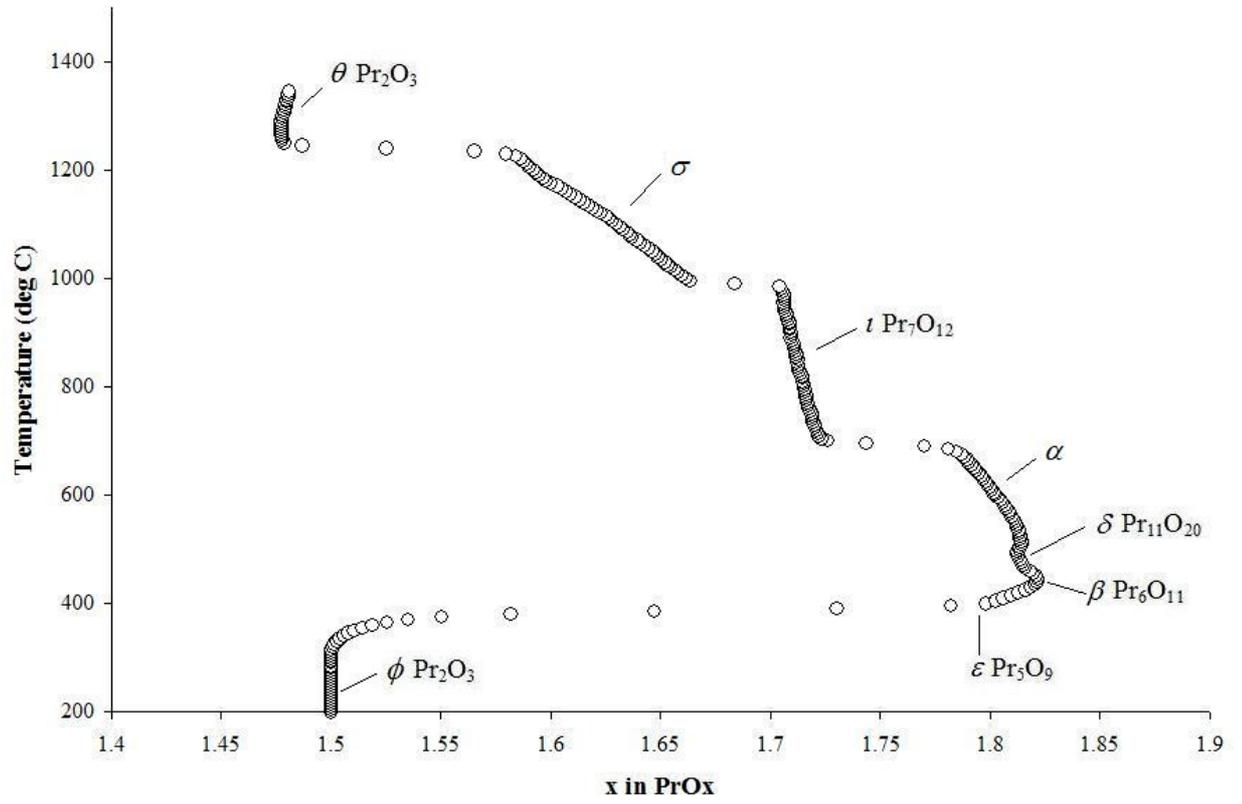
Figure 8.30 DSC recorded on sample (6) Pr₂O₃ at 2K/min in air with phases marked.

Figure 8.31 shows the paths through the phases, according to temperature.
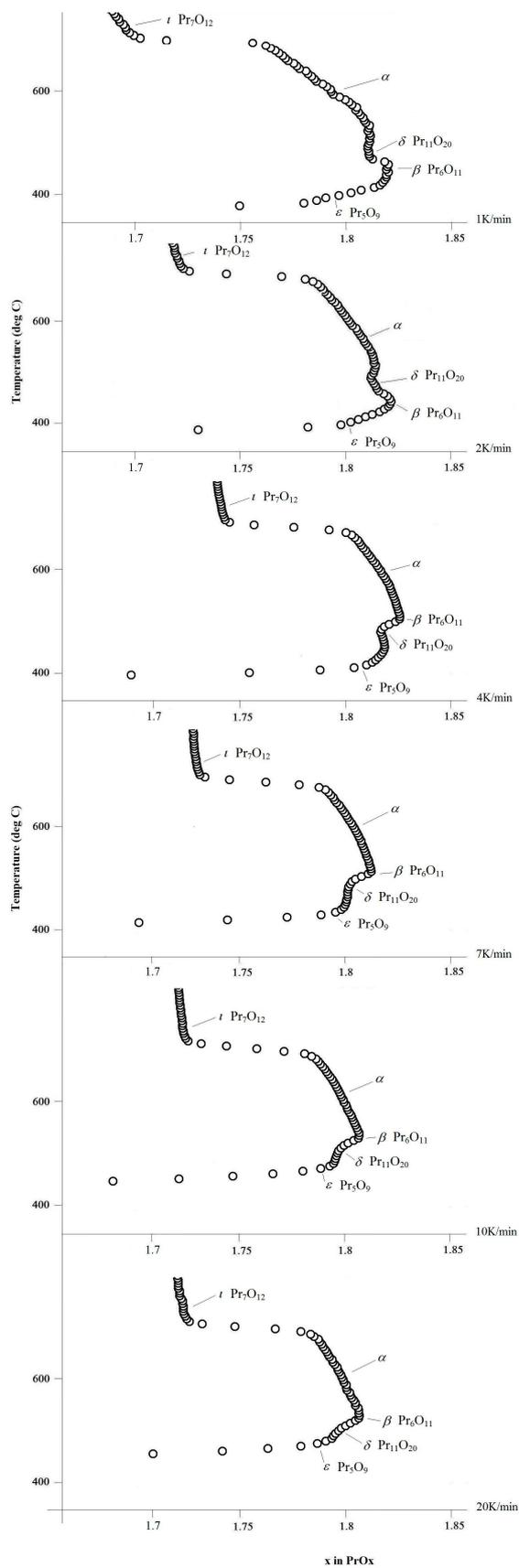
Figure 8.31 Phases attained during ramps on sample (6) Pr$_2$O$_3$.

Much of the temperature-composition diagram can be explained by the existence of discrete monophasic regions in the phase diagram, shown by little or no change in x with temperature. The only section of figure 8.29 that remains to be explained is the region between 1000°C and 1250°C. The region appears to correspond to the low oxygen boundary of the σ phase in the Pr-O phase diagram of figure 1.9. However, Hyde *et al* do not show oxygen composition above 1100°C. Also, the phase diagram does not show oxygen content above this temperature. A search through the PDF-2 database produced a reference for $PrO_{1.57}$ which is a cubic cell with the ceria structure, the oxygen sites being occupied only to 0.78. The material is described in the report as 'green brownish red'. This value of x is in the middle of the sloping line for this phase in figure 8.29 so it appears that the phase detected by DSC-TG is cubic. To support this, Hyde *et al* do state that their σ phase is cubic. It would be reasonable to assume that this line in figure 8.29 represents a continuity of stoichiometries and a slow release of oxygen from the cell. This is supported in the literature (Hyde *et al* 1965), (Adachi and Imanaka 1998). This data represents an addition to the existing phase diagram.

The change in the XRPD around 600°C (figure 7.36) can now be explained by the appearance of the ι phase, Pr_7O_{12}. The initial change from the hexagonal ambient phase to the cubic β phase is clear to see as it involves a change of cell type. However, many of the other Pr-O phase changes merely correspond to loss or gain of oxygen on the 8c Wyckoff sites of the ceria cell. These light atom changes are very difficult to detect using a laboratory diffractometer. It is only when the cell type again changes from the α phase (cubic) to the ι phase of Pr_7O_{12} (rhombohedral) that a change in the XRPD pattern is noticed. The phase change is shown as occurring at 625°C on heating and disappearing at 575°C on cooling. This point corresponds to the vertical section in the middle of the Pr-O phase diagram in figure 1.9 and also to region 4 in figure 8.29. Figure 8.32 shows the hysteresis loop for this transition.
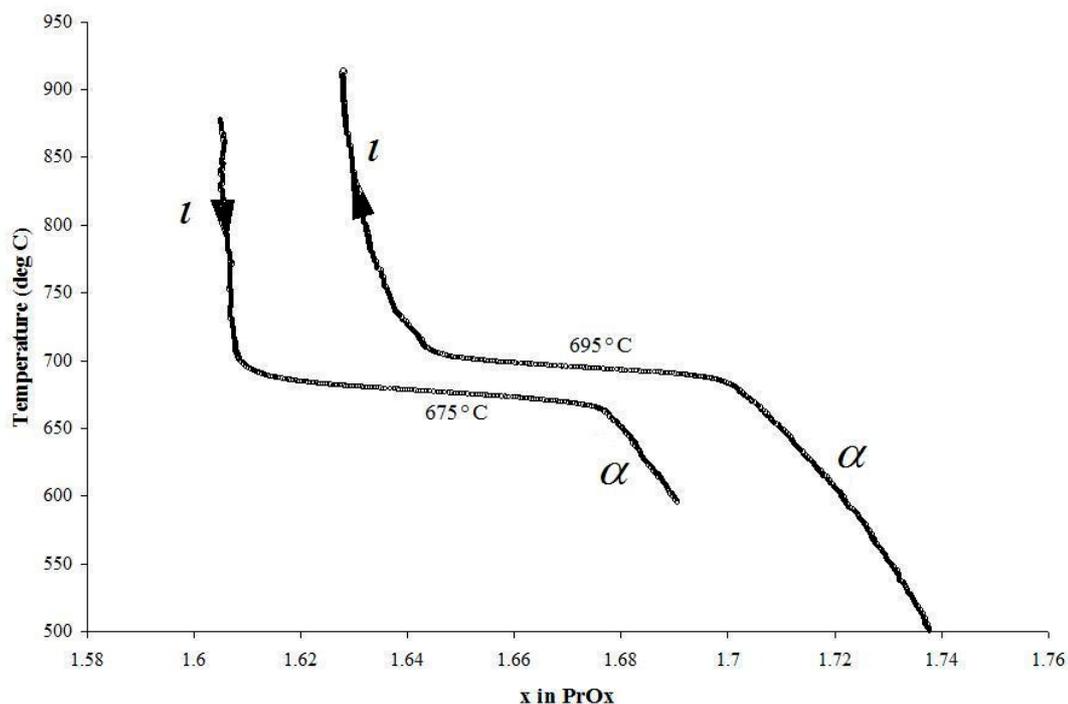
Figure 8.32 Hysteresis loop for the α phase to ι phase (Pr_7O_{12}) transition.

In a temperature-composition diagram, a vertical line typically indicates a monophasic region i.e. the presence of a discrete compound that is structurally highly-ordered, where heating and cooling paths are often coincident. A horizontal line, where there is a sudden change of composition with little change of temperature, typically indicates a diphasic region where heating and cooling paths are not expected to coincide. This is illustrated in figure 8.32. Sloping temperature-composition lines which are coincident on heating and cooling also indicate a monophasic region, but with a disordered and non-stoichiometric phase. Where heating and cooling paths are not coincident, a multi-phasic and non-stoichiometric region is inferred. The latter example is the case with the σ phase shown in the TG data, and illustrated in figure 8.33, below.
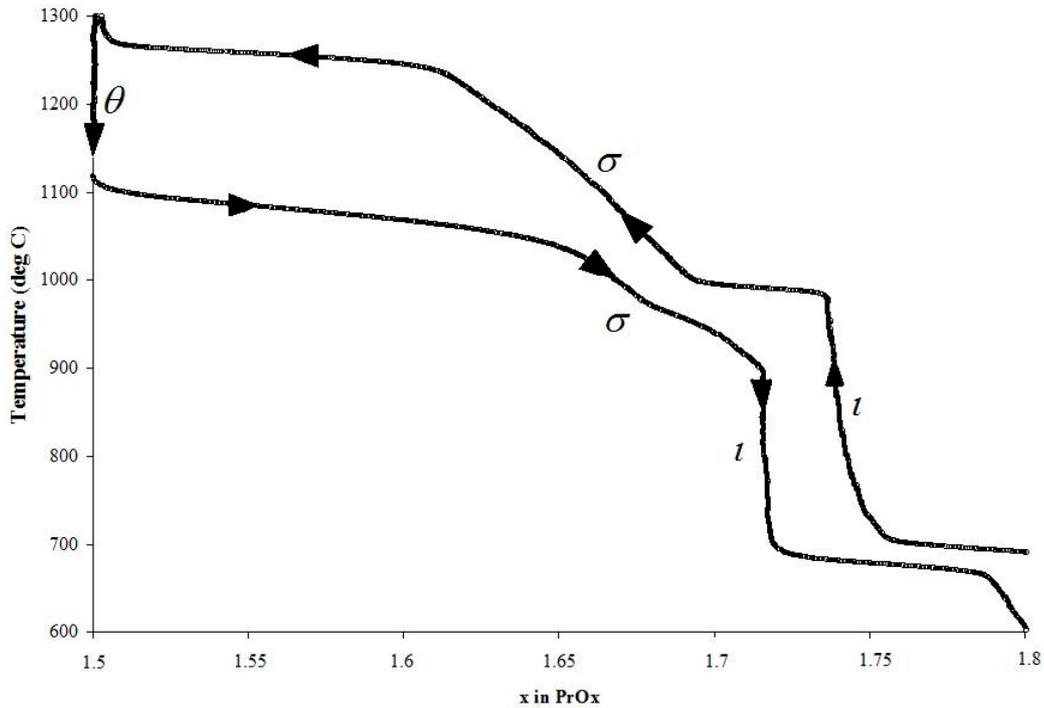
Figure 8.33 Temperature-composition plot for the ι-σ-θ region.

Other than the fact that there is some horizontal displacement between the heating and cooling plots, figure 8.33 shows that the path through the σ phase is not the same in both directions; on cooling, the sample oxidises rapidly below 1100°C to an oxygen composition of $x = 1.65$, rather than $x = 1.6$ which marked the low-oxygen end of the σ phase on heating.

8.8 COMPARISON WITH OTHER WORK

The δ ($x = 1.816$) phase is the most recently established (Hyde *et al* 1965) and these results have demonstrated its fleeting existence. In figure 8.31 it appears as a brief kink in the TG data either just before or just after the appearance of the β phase. This point in the data is most pronounced in the 2K/min and 4K/min runs. The kink which appears to mark the ε phase is less pronounced., and does not appear in the 1K/min and 2K/min runs. Hyde and co-workers only found the δ phase at low pressure, during the 45mm Hg run. They also note the ease with which oxygen is exchanged between solid PrO_x and the gas phase. This is confirmed by the close grouping of the ε, β and δ phases in

figure 8.29 and the corresponding lack of change in the XRPD in this temperature region (figure 7.35).

Hyde *et al* performed 4 heating experiments on praseodymium oxide at different pressures. They found that the order of appearance of phases changed with pressure. For example, in the run at 10mm Hg, the phases were ε (<497°C); ζ appearing at 497°C; ι appearing at 588°C; σ appearing at 906°C and showing the range $1.65 \geq x \geq 1.60$; and θ appearing at 1068°C. However, the run at 45mm Hg, which began with the β phase, showed the δ phase occurring briefly between the β and ε phases. For the run at 650mm Hg, the closest to that in this work (atmospheric pressure), the β phase existed below 300°C; rather than δ and ε, the α phase appeared at 470°C; ι appeared at 795°C; σ existed between 1065°C and 1150°C; and ι reappeared on cooling at 1069°C. In this thesis the only significant change between the different ramps was the order of appearance of the β and δ phases. The general pathway of Hyde *et al* (β - α - ι - σ) is in partial accord with the results in this work (ε - β - δ - α - ι - σ). However, my work also appeared to show the existence of the ε and δ phases at ambient pressure, contrary to the results of Hyde *et al*.

Hyde *et al* note the coincidence of heating and cooling curves for the higher oxygen content phases (β, δ, ε and ξ), but not for the higher temperature transitions. In this thesis, this pattern was noted. At 10mm Hg they noted the lack of the σ phase on cooling, the θ phase converting directly into the ι phase. In general, their heating and cooling curves at high temperature were not coincident. They attribute this to the presence of a mixed θ and σ phase at the point of commencement of cooling, with the σ phase immediately starting to oxidise on cooling but the θ phase not oxidising until a break temperature of about 1050°C. Their isobaric runs are shown in figure 8.34.
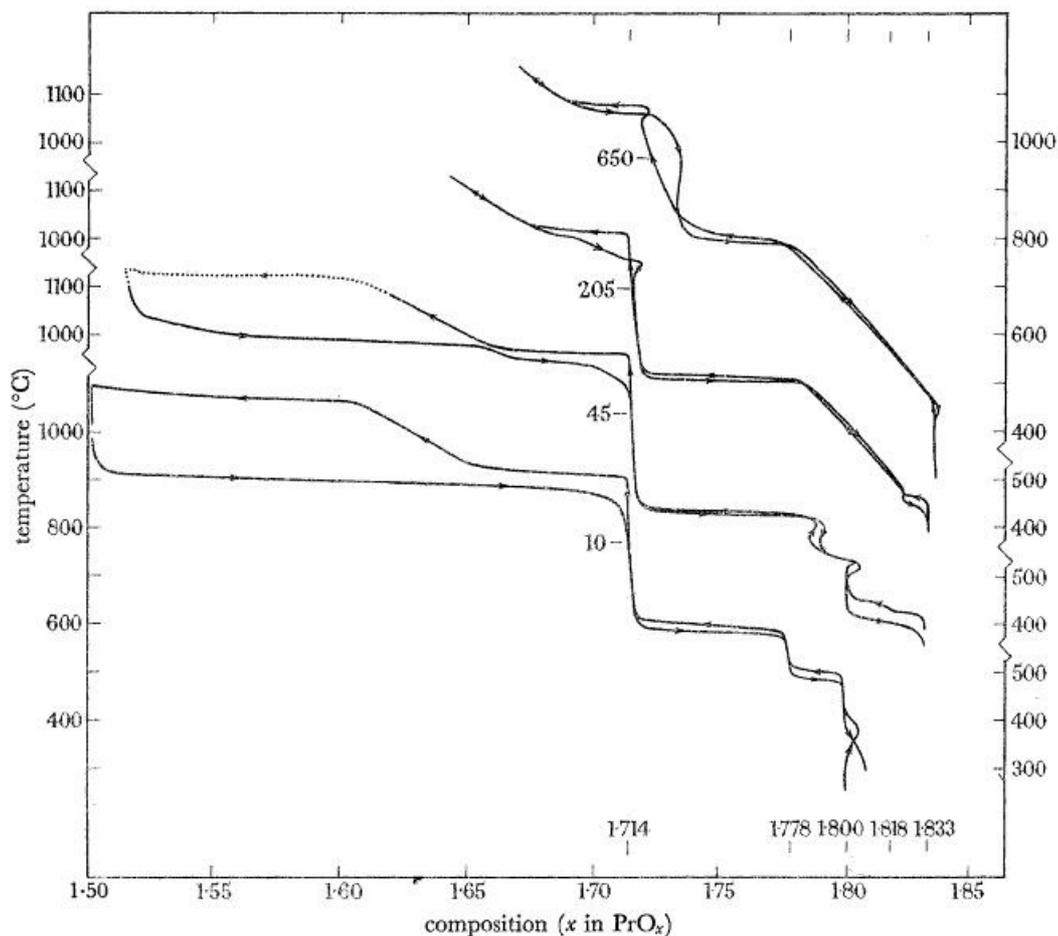
Figure 8.34 Isobaric runs on Pr_2O_3. Figures against curves indicate pressure in mm Hg (Hyde et al 1965).

This behaviour has been observed by others (Sonström 2010). A similar divergence of curves was noted in my work. Figure 8.33 clearly shows a different pathway for θ - σ - ι on heating than on cooling, confirming the hysteresis. Additionally, the run of Hyde *et al* carried out at 650mm Hg shows different ascending and descending curves for the ι - σ boundary. In their paper this is the only pressure at which this occurs, all other runs showing coincident curves. The work in this thesis was done at a similar pressure and shows a similar divergence.

Finally, Hyde *et al* note the appearance of ε and ζ only at low pressure; they appear in the 10mm and 45mm Hg runs as vertical sections. However, in the 205mm and 650mm Hg runs the prominent feature in this region is a sloping line indicating the α phase. The appearance of α (and the consequential absence of ζ) was a prominent feature of

the work in this thesis. However, contrary to the work of Hyde *et al*, the ε phase does appear to be present in the images of figure 8.31.

Although there have been many studies on the Pr-O system, there have been very few kinetic studies, as already mentioned in chapter 7. One study (Inaba *et al* 1980) looked at the conversion between the ξ and ι phases over the temperature range 535-570°C and obtained a value of 189.7kJ.mol^{-1} for the activation energy. A second study (Hyde *et al* 1965) studied oxidation of the β phase to the dioxide in the range 265-307°C, obtaining a value of 112.6kJ/g-atom of O for the activation energy. Figure 8.32, which shows the ι - α transition, is consistent with the historical work on this phase transition (Inaba *et al* 1981). This reference demonstrated a reproducible hysteresis loop with varying oxygen pressure and an activation energy of 60.9kcal.mol^{-1} (255.0kJ.mol^{-1}) on reduction and 75.0kcal.mol^{-1} (314.0kJ.mol^{-1}) on oxidation. Although it was not possible to determine the activation energy from the DSC-TG data in this thesis, this value appears consistent with the other values for phase changes in this system. The authors noted an inflexion in the hysteresis loop at $PrO_{1.75}$, although this was not observed in my work.

The activation energy values obtained in my work were -154(7) kJ.mol^{-1} (avg) for the ϕ to β phase transition, occuring between 368°C and 460°C and 1224(122) kJ.mol^{-1} for the σ to θ phase transition, occuring between 1224°C and 1273°C. These are tabulated below together with the historic values.

Transition	Temperature range (°C)	EA (kJ.mol^{-1})
$\phi \rightarrow \beta$	368 to 460	-154(7) avg
$\beta \rightarrow PrO_2$	265 to 307	112.6kJ/g-atom of O[1] Equivalent to 306.3
$\xi \rightarrow \iota$	535 to 570	189.7 (oxidation)[2]
$\alpha \leftrightarrow \iota$	655 to 715	255.0 (reduction) 314.0 (oxidation)[3]
$\sigma \rightarrow \theta$	1224 to 1273	1224(122)

Table 8.12 Kinetic data for the Pr-O system.

[1] *(Hyde et al 1965)* [2] *(Inaba et al 1980)* [3] *(Inaba et al 1981)*

Although the available data is limited, there is a correlation between temperature of phase change and activation energy. Encouragingly, the value of -154(7) kJ.mol^{-1} obtained for the $\phi \rightarrow \beta$ transition agrees with that obtained in Chapter 7 via XRPD data.

9 CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

9.1 SUMMARY

This work has demonstrated the following:

(i) the high-temperature phases of some lanthanoid oxides can be quenched to ambient temperature, contrary to the phase diagram;

(ii) structural modifications exist which are not indicated by the phase diagram;

(iii) high-temperature phases may already exist in commercially available samples, contrary to the supplier's information;

(iv) kinetic data in the Pr-O system obtained via different sources show correlation, and activation energies are generally much lower than for the sesquioxides;

(v) phase pathway can depend upon heating rate;

(vi) indexing of XRPD data is not straightforward and it is not even guaranteed that high-symmetry cells will always index;

(vii) it is possible to index a cell from limited XRPD data when the Bragg reflections contribute only a small fraction to the overall diffraction wave envelope;

The above summary is detailed in the following sections.

9.2 LANTHANIDE OXIDE CRYSTAL STRUCTURES

The phase diagram for the sesquioxides shown in figure 1.5 indicated that no monoclinic phases were present at ambient temperature. However, it was immediately found that the commercially-obtained sample of europia already contained a small quantity of the B-type phase. More surprisingly, samaria contained 97% B-type phase, even though the supplier stated the cell type to be cubic. The metastability of B-type europia was demonstrated by heating to 1334°C, holding for 1 hour and cooling slowly. The short anneal time and lack of quenching were expected to be detrimental to the creation and retention of the B-type phase. However, it was shown that monoclinic europia is relatively easy to generate and stable enough for the bulk material to

maintain 100% B phase on standing. Figure 1.5 indicates a higher temperature is required to perform the same treatment on gadolinia. In practice it took significantly more energy than was expected in order to force the change. Considering the sample of gadolinia was heated over 160ºC higher than the sample of europia and also cooled rapidly it seemed reasonable to predict that a significant proportion of monoclinic structure should have been retained. However, this was not the case. An anneal for 7 hours at 1500°C was required to completely transform the structure. Again, this change was maintained in the bulk material, and long enough for it to be posted to Diamond Light Source. A 5-hour run at the same temperature led to the creation of 97% B phase; clearly the reaction in gadolinia requires considerably more energy than for europia. Both the laboratory and synchrotron data allowed the previously unpublished structure of monoclinic gadolinia to be determined.

To demonstrate whether B-type gadolinia was as stable as B-type europia, an XRPD pattern on the sample used in figure 7.21 was taken 5 months later. The phase fractions were found to have stayed the same, showing that B-type gadolinia, too, may persist at ambient temperature.

Because of lack of facilities it was not possible to determine the structure for B-type Yb_2O_3. However, the cell type was shown to be monoclinic, again demonstrating the existence of a phase contrary to figure 1.5. The energy required to force the change in ytterbia is so high that either melting and quenching, or in situ XRPD, would be required to demonstrate the structure. Whatever conversion was achieved in the furnace at 1500°C, after quenching only 1% B phase was detected. The presence of B-type Yb_2O_3 after heating to a relatively low temperature is contrary to recent work (Guo, Harvey *et al* 2007), (Meyer *et al* 1995). The former reference states that flame synthesis at high temperature (up to 2800°C) and ambient temperature, followed by rapid cooling, is necessary to create the monoclinic phases of Er_2O_3, Tm_2O_3 and Yb_2O_3, and that lower temperature (2680°C) only led to the cubic phases. Meyer *et al* state that a temperature of 2000°C is not sufficient for the B-type structure to be attained. My work has shown that heating in a laboratory bench-top furnace to 1500°C will create a small amount of B-type Yb_2O_3 in the bulk material. Reflecting my results, Sun and co-workers (Sun *et* al 2007) were able to identify the cell type from a residue of

monoclinic lutetia existing within an otherwise cubic sample, but state there are high uncertainties in the recorded lattice parameters.

Although monoclinic ytterbia was present as a residue, the calculated lattice parameters compare favourably with those obtained historically. The cell reported in this work was $a = 13.740(2)$Å, $b = 3.400(2)$Å, $c = 8.593(2)$Å and $\beta = 100.12°$. Previously reported cells are $a = 13.73(1)$Å, $b = 3.425(3)$Å, $c = 8.452(8)$Å and $\beta = 100.17(5)°$ (Hoekstra 1966) and $a = 13.72$Å, $b = 3.428$Å, $c = 8.437$Å and $\beta = 100.18°$ (Coutures et al 1972).

It is noteworthy that the metastability of the B-type phases for the intermediate weight oxides and their existence at ambient temperature indicates that the phase diagram according to Foëx and Traverse is somewhat misleading. Such irreversibility of phase conversion was also seen in the Pr-O system with the ϕ to β phase change, occurring at only 275°C on heating. The actual pathway through the Pr-O phases appears to depend on heating rate, but the final phase is the θ phase. However, on cooling back, the β phase is the last to form i.e. the ϕ phase does not reappear. The activation energy of around -150 kJ.mol^{-1} for the $\phi \rightarrow \beta$ transition was found to be much less than that of the well-researched europium sesquioxide C $\rightarrow$ B transition, at 650 kJ.mol^{-1}.

9.3 INDEXING

Although the cubic gadolinia pattern indexed successfully using CRYSFIRE, those of europia and ytterbia did not. However, on relaxing the tolerance in the allowed 2θ difference between matching experimental and calculated lines, CRYSFIRE found the correct solutions. It is noted that reliance should always be placed on an accurately recorded pattern rather than a reduction in the strictness of the indexing parameters; it is all too easy to find a solution which appears to match the experimental data, when in fact it is not the correct solution. As an aside, to test the efficacy of the indexing programs, a set of theoretical Bragg reflections for a cubic cell were created and entered into CRYSFIRE; none of the indexing programs was able to find the correct solution.

It is notable that CRYSFIRE failed to index the B-type gadolina pattern. Had it not been for the fact that the cell parameters for europia were known, this would have been a serious obstacle to the determination of the crystal structure. It serves as an illustration that the indexing stage is the often the most problematic in the sequence and is also the most difficult and most time-consuming part of the process.

The lack of significant changes in the gadolinia and ytterbia patterns on heating was initially considered to be a stumbling block in the investigation of their monoclinic phases. However, it was decided to investigate just the lines which had appeared on heating. Surprisingly, by making assumptions about cell parameters and minimising the differences between the actual and calculated lines it was possible to estimate the cell parameters of the respective materials. It was, of course, not possible to carry out full profile refinement using GSAS because only a fragment of the monoclinic pattern was being observed and even then, the intensities were very low. But this exercise in 'forensic diffractometry' serves to show that it is possible to use limited information together with certain assumptions to determine crystal habit.

9.4 COMPARISON OF KINETIC DATA FROM XRPD AND DSC

Although some problems were experienced in obtaining kinetic data, most notably due to the mixed phase and gas contamination of sample (4) Pr_2O_3, there are definite correlations in the data. Analysis of isothermal holds using XRPD data gave activation energy values of $-149(10)$ kJ.mol^{-1}, $-146(2)$ kJ.mol^{-1} and $-154(2)$ kJ.mol^{-1} using 2 different methods for the ϕ to β phase transition. These values were supported by those obtained through DSC, which indicates the data to be accurate and obtained using sound methods. The kinetic data is summarised in table 9.1.

Sample	Low temp phase	Reaction	Feature	Method	EA (kJ.mol^{-1})
(4) Pr_2O_3	Cubic+hex	$\phi \rightarrow \beta$	47.2° peak	XRPD	-146(2) (ShSp[1])
					-154(2) (JMAK[2])
(4) Pr_2O_3	Cubic+hex	$\phi \rightarrow \beta$	41.4° peak	XRPD	-149(10) (ShSp[1])
(4) Pr_2O_3	Cubic+hex	$\phi \rightarrow \beta$[3]	1st endo	DSC	108(9)
(4) Pr_2O_3	Cubic+hex	$\phi \rightarrow \beta$[3]	2nd endo	DSC	103(6)
(4) Pr_2O_3	Cubic+hex	$\phi \rightarrow \beta$[3]	3rd endo	DSC	61(3)
(6) Pr_2O_3	Hex	$\phi \rightarrow \beta$	1st exo 450°C	DSC	152(8)
(6) Pr_2O_3	Hex	$\phi \rightarrow \beta$	1st exo 450°C	DSC	155(10)
(6) Pr_2O_3	Cubic	$\sigma \rightarrow \theta$	1250°C endotherm	DSC	1224(122)

[1] obtained via a Shrinking Sphere model   [2] obtained via JMAK model

[3] Believed to proceed as $Pr(OH)_3 \rightarrow Pr_2O_3 \rightarrow Pr_6O_{11}$

Table 9.1 Comparison of activation energy data from XRPD and DSC.

Had facilities continued to be available, it would have been useful to compare the activation energy value of approximately -150 kJ.mol^{-1} for praseodymia with those for nedodymia, samaria and europia via DSC and to then relate these to the values obtained historically by Stecura and Ainscough. Table 9.2 shows the values obtained above with these historical values.

Oxide	Ambient phase	Reaction	Method	EA (kJ.mol^{-1})
(4) Pr_2O_3	Cubic+hex	$Pr_2O_3 \rightarrow Pr_6O_{11}$	XRPD	-146(2) (ShSp[3])
(4) Pr_2O_3	Cubic+hex	$Pr_2O_3 \rightarrow Pr_6O_{11}$	XRPD	-154(2) (JMAK[4])
(4) Pr_2O_3	Cubic+hex	$Pr_2O_3 \rightarrow Pr_6O_{11}$	XRPD	-149(10) (ShSp[3])
(6) Pr_2O_3	Hex	$Pr_2O_3 \rightarrow Pr_6O_{11}$	DSC	-152(8)
(6) Pr_2O_3	Hex	$Pr_2O_3 \rightarrow Pr_6O_{11}$	DSC	-155(10)
Nd_2O_3	Cubic	C type $\rightarrow$ A type	XRPD	502[1]
Sm_2O_3	Cubic	C type $\rightarrow$ B type	XRPD	628[1]
Eu_2O_3	Cubic	C type $\rightarrow$ B type	XRPD	691[1]
Eu_2O_3	Cubic	C type $\rightarrow$ B type	XRPD	493[2]
Gd_2O_3	Cubic	C type $\rightarrow$ B type	XRPD	787[1]

Table 9.2 Activation energies for the lanthanide oxides.

[1] (Stecura 1966)   [2] (Ainscough *et al* 1975)

[3] obtained via a Shrinking Sphere model.   [4] obtained via JMAK model

Had the diffractometer hot stage been able to reach a higher temperature than 800°C, two further changes in the XRPD patterns would be expected. These would be the ι phase changing to the σ phase around 1000°C and finally the σ phase changing to the A-type (θ phase) sesquioxide at 1200°C. The access to a diffractometer capable of reaching 1500°C would enable a more detailed study of the Pr-O phase diagram; it is

the high-temperature and low-oxygen region of the diagram that is lacking in information.

9.5 COMPARISON OF DSC-TG DATA WITH HISTORIC DATA

The 2 transitions for which kinetic data were obtained in my work ($\phi \rightarrow \beta$ and $\sigma \rightarrow \theta$) do not appear to have been investigated previously. The data presented in chapter 8 is repeated below, including the historic data for the $\beta \rightarrow PrO_2$, the $\xi \rightarrow \iota$ and the $\alpha \leftrightarrow \iota$ transitions.

Transition	Temperature range (°C)	EA (kJ.mol^{-1})
$\phi \rightarrow \beta$	368 to 460	-151(16) avg
$\beta \rightarrow PrO_2$	265 to 307	112.6kJ/g-atom of O[1] Equivalent to 306.3
$\xi \rightarrow \iota$	535 to 570	189.7 (oxidation)[2]
$\alpha \leftrightarrow \iota$	655 to 715	255.0 (reduction)[3] 314.0 (oxidation)[3]
$\sigma \rightarrow \theta$	1224 to 1273	1219.9

[1] *(Hyde et al 1965)* [2] *(Inaba et al 1980)* [3] *(Inaba et al 1981)*

Table 9.3 Kinetic data for the Pr-O system.

Whilst there is little kinetic data against which to review the results from this thesis, the transitions in the high oxygen composition of the phase diagram are all considerably less than those involving the C $\rightarrow$ B phase transitions in the sesquioxides. It is known that the activation energies for the C $\rightarrow$ B transformation in the intermediate weight oxides are in the range 500 to 800kJ.mol^{-1} (Stecura 1966). It should be expected that activation energies in the high oxygen region of the Pr-O system would be significantly less, because of the ease with which oxygen exchanges between the solid and the gas phase and indeed this is the case with the above data.

There were two notable results from the DSC-TG work on Pr-O. Firstly, the exact pathway through the phases appears to depend upon heating rate. Figure 8.31 shows that for the slower heating rates (2K/min and 1K/min) the pathway for ascending temperature is $\phi \rightarrow \varepsilon \rightarrow \beta \rightarrow \delta \rightarrow \alpha \rightarrow \iota \rightarrow \theta$. However, for the faster ramps (20K/min down to 4K/min), the pathway is $\phi \rightarrow \varepsilon \rightarrow \delta \rightarrow \beta \rightarrow \alpha \rightarrow \iota \rightarrow \theta$ i.e. the appearance of β and δ are reversed. The former path is the expected one when considering the temperature range through which the species occur in the phase diagram (figure 1.9).

However, it appears that for this to be observed, a slow and prolonged input of heat is required. Secondly, Eyring and his co-workers were only able to demonstrate the existence of the ε phase up to 45mm Hg pressure, and yet it appears to be present in the 4, 7, 10 and 20K/min ramps of figure 8.31, recorded at atmospheric pressure. The appearance of the ε phase in the DSC-TG data was always slight, being no more than an inflexion in the curve, although its prominence increased with temperature ramp. However, it does seem reasonable that its existence at ambient temperature is possible, since the other two phases in this close triplet (β and δ) are merely the same structure but with different oxygen content.

9.6 REDRAWING THE PHASE DIAGRAMS

Table 9.4 lists the temperatures of phase transformations in Ln_2O_3 recorded historically and also in this work.

Oxide	Phase change	Temperature (°C)	Author
La_2O_3	$C \rightarrow A$	450	Stecura[1]
Nd_2O_3	$C \rightarrow A$	850-1050	Stecura[1]
Sm_2O_3	$C \rightarrow B$	950-1100	Stecura[1]
Eu_2O_3	$C \rightarrow B$	1072-1347	Beljaev[2]
		1334	My work
		1297	Sun et al[3]
		1050-1300	Stecura[1]
		1175-1200	Ainscough et al[4]
		1127	Antic et al[5]
Gd_2O_3	$C \rightarrow B$	1334-1500	My work
		1397	Sun et al[3]
		1260-1400	Stecura[1]
Yb_2O_3	$C \rightarrow B$	1500+	My work

[1] (Stecura 1966) [2] (Beljaev 1974) [3] (Sun et al 2003) [4] (Ainscough et al 1975) [5] (Antic et al 1997)

Table 9.4 Temperatures of phase transformations in Ln_2O_3.

To reflect the data in table 9.3, the phase diagram in figure 1.5 has been redrawn below.
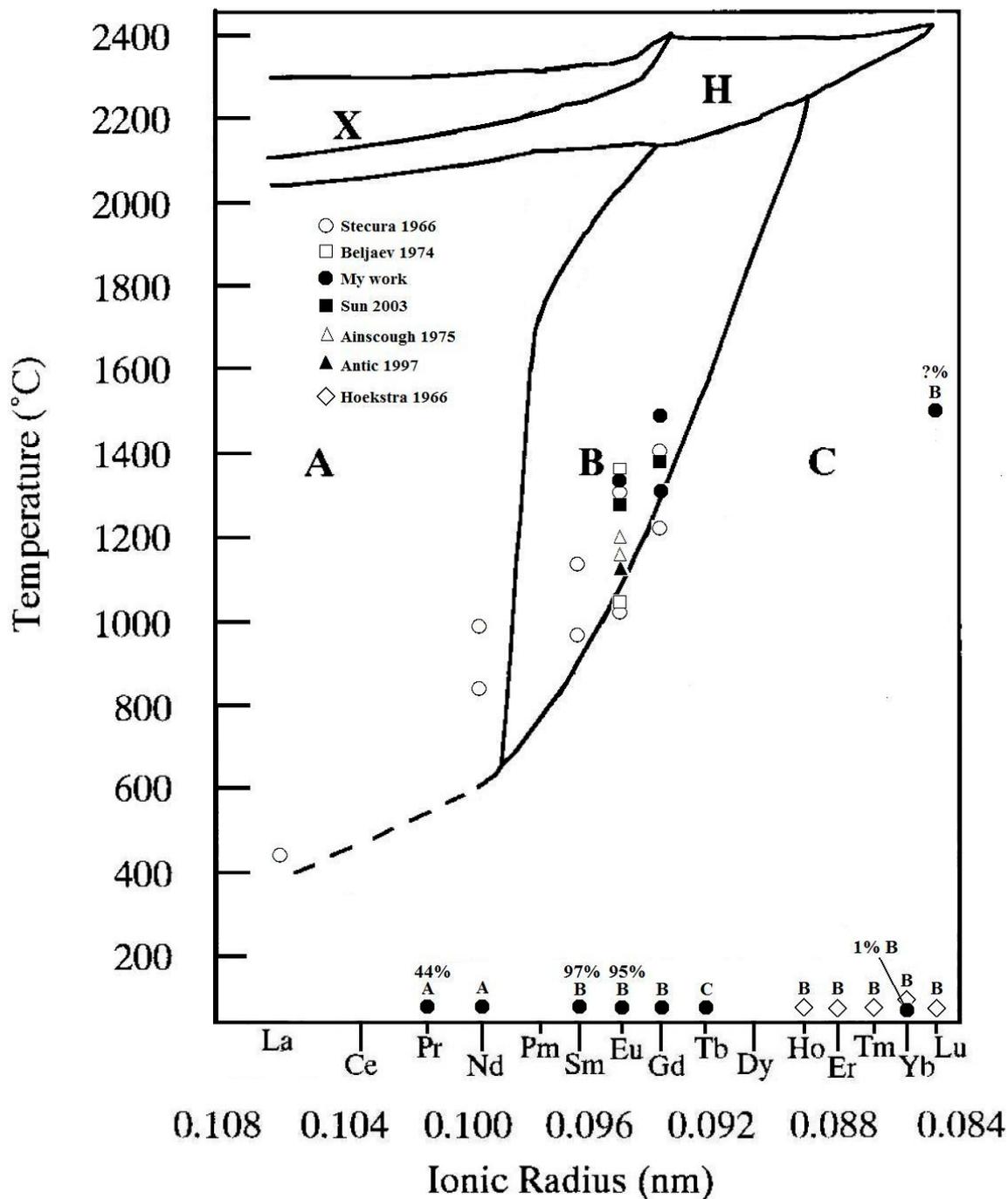
Figure 9.1 Amended phase diagram for the lanthanide sesquioxides.

Where conversion temperatures are stated, much of the work following that of Foëx and Traverse is consistent with figure 1.5 i.e. the data follows the C → B boundary. However, there are discrepancies. It has been demonstrated that it is possible to flame synthesise and quench monoclinic Er_2O_3 from 2800°C (Guo, Harvey *et al* 2007). Monoclinic erbia has also been created between 9.9 and 16.3GPa at 1000°C and

quenched (Guo, Zhao *et al* 2007). Yet in figure 1.5 Er_2O_3 is clearly shown as having no B-type phase. My work has shown that a small percentage of Yb_2O_3 was present after heating for 5 hours at 1500°C and quenching. The percentage conversion at this temperature is not known, but it is clear that phases exist contrary to the phase diagram. What is needed is an estimate for where the C $\rightarrow$ B boundary continues after Gd_2O_3. Looking at Stecura's data, the temperature range across which the transformation occurs to any degree decreases with increasing atomic number of the lanthanide. For example, the range for Nd_2O_3 is 200 degrees and for Gd_2O_3 it is 122 degrees. Assuming a linear relationship and extrapolating to Yb_2O_3 gives a value of approximately zero for the range. Clearly this is not reasonable, as we would expect some kinetic element to any data collected. However, it may be that the range is indeed very narrow. With only one data point collected in my work it is not possible to draw the new boundary, but it must encompass the point at 1500°C recorded in section 7.2 with Yb_2O_3. It may be that it also encompasses the oxide Lu_2O_3.

Also of note is the stability of many of the B-type oxides. My work has shown that monoclinic Eu_2O_3 and Gd_2O_3 are stable at ambient temperature i.e. the reaction is not reversible. The commercial sample of Eu_2O_3 already contained a trace of B-type phase and the sample of Sm_2O_3 contained 97% B-type phase, contrary to the supplier's information. The existence of heavier oxides at ambient temperature after heating to 2800°C and quenching has been demonstrated (Guo, Harvey *et al* 2007).

The work in chapter 8 did allow a study of the existence of the σ phase of Pr-O above the temperature reached by Hyde et al and figure 9.2 shows this pathway.
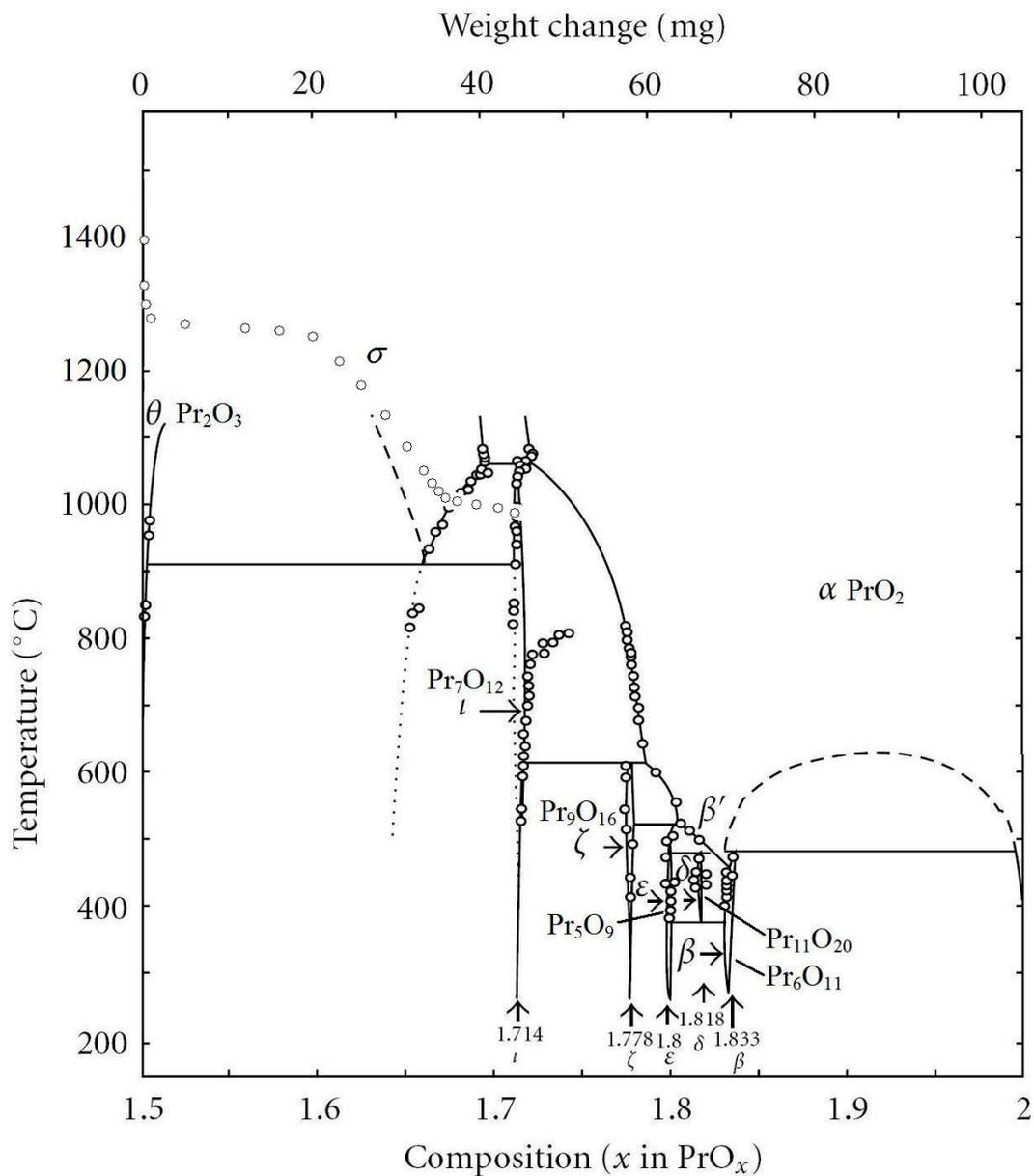
Figure 9.2. Amended phase diagram for the praseodymium-oxygen system showing the σ phase.

9.7 SUGGESTED FUTURE WORK

The most pressing work must be the obtaining of DSC data for Nd_2O_3, Sm_2O_3 and Eu_2O_3 to enable a kinetic study. The results could then be compared to those of Ainscough and Stecura and to the boundary line for the cubic-monoclinic interface in figure 1.5.

The monoclinic forms of the heavier lanthanide sesquioxides (Sm-Yb) are now all known to exist. Heating ytterbia for longer in a furnace and quenching is a possibility but considering the phase diagram in figure 1.5 the XRPD pattern might need to be recorded in situ. If this were possible then a kinetic study could be made. It would also enable the redrawing of the C → B boundary. However, such facilities are rare and the intense conditions detrimental to the sample environment. An alternative would be to melt and fuse the material in an oxy-acetlyene flame, grind up the cooled solid and run the pattern again, on the assumption that it would remain stable back to ambient temperature. Monoclinic Sm_2O_3 has been obtained by this method (Douglas and Staritsky 1956), although of course the stability of samaria at ambient temperature would be far greater than that of B-type ytterbia. However, there is a possibility that the B phase of ytterbia might be locked in on fusing and even if 100% conversion is not retained, there may be enough product phase present to enable the atom positions to be determined. That monoclinic Er_2O_3 was quenched to ambient conditions (Guo *et al* 2007) gives reason to believe that it may be possible with Yb_2O_3.

Regarding the existence of the ε phase, the conflicting work of Eyring *et al* with figure 8.31 warrants further investigation. It appears that a fast heating rate is needed to more clearly show the transition from the ϕ phase. The work in 6.3.1.4 could be repeated, and augmented with ramps at, say, 30K/min and 40K/min, which is the limit of the machine. Also, XRPD patterns could be recorded at a much faster heating rate to identify any change in the Bragg reflections attributable to the ε phase. A characteristic region of 2θ would need to be identified in order to greatly reduce the counting time and allow the temperature to be changed more rapidly. Alternatively, the machine could be pre-heated to the required temperature and the sample mounted directly into a hot environment.

There exists the possibility of studying other series of compounds in which the recorded powder diffraction patterns and/or structures are not available. Compounds of the lanthanides are of particular interest because of the steady contraction in cell size that is seen across any particular series. This is a reflection of the lanthanide contraction of ionic radius across the series of tripositive lanthanide ions. This feature of lanthanoid

compounds means it is often possible to predict the structure of an unprepared species based on the structures of its neighbours in that particular series.

There are some absences in the anhydrous lanthanoid trichlorides. The members of the series $LnCl_3$ are hexagonal from lanthanum to gadolinium. From terbium onwards there are hexagonal, tetragonal and orthorhombic structures present. However, from analysis of the Daresbury database, no crystal structures appear to have been recorded for the trichlorides of samarium, holmium, erbium, ytterbium and lutetium. In the PDF-2 database there are cell parameters for all except $HoCl_3$.

A review of the efficacy of the indexing programs within the CRYSFIRE suite would be of interest. It had been demonstrated in my preliminary work that the programs can often fail even for XRPD patterns of high symmetry (even cubic) systems.

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ICSD Daresbury Laboratory ICSD crystal structure database originally hosted at http://cds/dl/ac/uk

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